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Surface functionalization of crystalline silicon substrates

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SURFACE FUNCTIONALIZATION OF CRystalline Silicon SUBstrates

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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By
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ABSTRACT

In this work, various chemical and electrochemical methods were demonstrated to attach application-specific organic monolayers to crystalline silicon substrates. In one study, alkyl (CH₃, C₂H₅) monolayers were anodically electrografted or thermally grafted onto planar (100) silicon substrates using Grignard precursors. The results show electrografted methyl monolayers provide a stable Si-C termination, resisting oxidation on (100) surfaces for approximately 55 days in air. The alkyl termination could provide a potential alternative to defective native oxides and kinetically unstable hydride surfaces. A mechanism involving two electron transfers per grafting event was established for both the thermal and electrochemical routes. In another study, unsaturated organic functional groups (phenylacetylene, 5-hexynoic acid) were cathodically electrografted onto planar (100) silicon substrates. Although cathodic grafting mechanism is considerably different, its voltammetric behavior (hysteresis, onset potential shifts) appears similar to anodic grafting process. Experimental results show both anodic and cathodic grafting methods may be applied to pattern the silicon surfaces in situ. Dielectric templates such as polystyrene microspheres or polydimethylsiloxane stamps were used to obtain high throughput, nanoscale monolayer patterns on silicon surfaces. The patterned monolayers may be further used to immobilize biological enzymes via 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) chemistry or to direct selective copper electrodeposition or etching on silicon. Established grafting mechanisms were applied to functionalize nanoscale silicon anodes in lithium batteries to improve capacity retention with charge/discharge cycling.

Silicon anodes present a safe, high-capacity alternative to conventional carbonaceous anodes; however, a significant capacity loss (>20% initial value) is observed within the first few cycles, primarily due to 300% volume expansion upon lithiation. Silicon nanowires with atleast
one dimension <300 nm may withstand the volume expansion effects but may not completely eliminate the capacity fade. This residual fade is mainly a result of protective solid electrolyte interphase (SEI) layer formed on the anode surface due to electrolyte dissociation. Various ex situ and in situ functionalized silicon surfaces were investigated to establish engineered silicon-SEI interface with improved chemical, mechanical and electrical aspects. The work shows silicon lithiation is a function of surface chemistry and in situ methyl siloxane functionalization offers improved capacity retention with nanoscale silicon anodes in lithium batteries.
1. SURFACE FUNCTIONALIZATION OF SILICON

1.1 Introduction

An ability to maneuver silicon surface chemistry with organic terminal groups unlocks variety of applications such as microelectronics,(Nemanick, Hurley et al. 2006) biosensors,(Scheibal, Xu et al. 2008) lithium battery anodes,(Chan, Peng et al. 2008; Xu and Flake 2010) etc. Silicon surfaces are typically covered with a native oxide (<5 nm thick) layer when exposed to ambient air. Native oxides include many sub-oxides, and defects(Buriak 2002) and are typically replaced by a thermally grown oxide layer for microelectronics applications. Furthermore, oxides are not considered ideal for many sensing or photoelectrochemical applications due to relatively high defect density, high recombination velocity (>100 s\(^{-1}\)) and screening effects (Debye).(Buriak 2002) For most applications, the native oxide layer is replaced by a surface hydride termination via treatment with hydrofluoric acid (HF);(Buriak 2002) however, the hydride surfaces are highly reactive and native oxide formation initiates within a few hours in air or any oxide-rich environment. Relative to hydride termination, organic functionalization offers better stability, passivation towards nucleophilic substitution reactions and lower bond polarity to silicon surface, besides presenting versatile application-specific functional groups such as acid, alkyl, amine, ester, etc. In this work, application-specific silicon surface functionalization is demonstrated to address robust challenges in the fields of gate dielectrics, patterned resists, bioimmobilization and silicon anodes in lithium batteries.

Organic functionalization of silicon may be classified into two types, indirect (Si-O-Si-R) and direct (Si-R) monolayers anchored by Si-O-Si-C and Si-C surface bonds respectively as shown in Figure 1.1.
Figure 1.1 Schematics for hydride, indirect Si-O-Si-R and direct Si-R terminations on (100) silicon surfaces.

Indirect (Si-O-Si-R) bonds may be achieved by treating the silicon surfaces with self-assembling siloxane precursors (typically $X_3$-$Si$-$R_1$ or $R^2$-$O$-$Si$-$R_1$, where $X =$ halide, $R^2 =$ alkyl and $R^1 =$ organic functional group) to create compact monolayers or cross-linked multilayers. The self-assembled siloxane monolayers may be covalently bonded to oxide or hydroxyl terminated silicon surfaces through spontaneous (<1 minute) condensation reactions. (Koelling and Kolb 1965; Dunaway and McCarley 1994) Relative to indirect (Si-O-Si-R) bonds, direct (Si-R) bonds are thermodynamically and kinetically stable. (Nemanick, Hurley et al. 2006; Amy, Michalak et al. 2007) do not require
underlying oxides or hydroxides and help retain crystalline order without point defects. (Diao, Guo et al. 2001; Valiokas, Svedhem et al. 2001)

Direct (Si-R) monolayers may be obtained via activation of unsaturated (Robins, Stewart et al. 1999; Sieval, Opitz et al. 2000; de Smet, Zuilhof et al. 2005) or reactive (Nemanick, Hurley et al. 2006; Nemanick, Hurley et al. 2006; Yamada, Shirasaka et al. 2006) precursors that in turn react with the silicon surface to create surface Si-C bonds. Various techniques such as chemical, (Schmeltzer, Porter et al. 2002) thermochemical, (Teyssot, Fidelis et al. 2002) photochemical (Faucheux, Gouget-Laemmel et al. 2006) or electrochemical (Robins, Stewart et al. 1999; Koiry, Aswal et al. 2007) pathways (Stewart and Buriak 2002; Shirahata, Hozumi et al. 2005) have been demonstrated to activate unsaturated or reactive precursors and create uniform direct Si-R monolayers on silicon surfaces. Figure 1.1 shows the schematics for hydride, indirect Si-O-Si-R and direct Si-R monolayers formed upon (100) silicon surfaces.

1.2 Oxide, Hydroxyl and Hydride Terminations

Crystalline silicon surfaces are typically obtained in (100), (111) and (110) orientations with native oxide termination. (Buriak 2002) Microelectronics offered initial exposure to silicon surface chemistry in need of a semiconductor/insulation interface for gate dielectric applications. Naturally formed native oxide via exposure to oxygen-rich environment and chemically formed silicon oxide via boiling in peroxide solutions may present required insulation but are non-uniform. Thermal oxidation technique provided a better alternative to native and chemical oxides with uniform insulation and relatively less defects in the interface. Thermal treatment typically incorporates a temperature range
of 700-1300 °C with either dry (oxide) or wet (humid) environment resulting in silicon oxidation as shown in reactions 1.1 and 1.2.(Deal and Grove 1965)

\[
\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \quad \text{dry oxidation} \quad (1.1)
\]

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2 \quad \text{wet oxidation} \quad (1.2)
\]

The thermally oxidized surfaces offer controlled oxide thickness as a function of exposure time, temperature and furnace atmosphere (dry or humid)(Deal and Grove 1965); however, the insulative thermal oxide layer still suffers from Debye and defect limitations(Buriak 2002) besides usage of toxic HF to remove the dielectric layer. The limitations of thermal oxide dielectric layer demanded novel research routes to obtain a stable, dense and defect-free silicon surface functionalization.

Treatment with hydrofluoric acid replaces the native oxide on silicon surface with a hydride termination; however, the uneven nature of native oxide precursor surface would result in a series of mono-, di- and tri-hydride termination on silicon surfaces.(Chabal, Higashi et al. 1989) A buffered oxide etch solution (BOE, 4:1 hydrofluoric acid: ammonium fluoride) may be used to replace the native oxide to yield atomically flat, mono hydride on (111) surfaces and dihydride on (100) surfaces.(Buriak 2002) The difference in hydride to silicon surface atomic ratio is mainly due to the bivalent nature of (100) silicon surfaces relative to monovalent (111) silicon surfaces. The mono-, di-, or tri-hydride terminations do not offer kinetic stability against oxidation, as the surface lasts only a few hours in an oxygen-rich atmosphere, before allowing native oxide formation again. Relative to hydride termination, organic monolayers on semiconductive silicon render kinetic stability with lower bond polarity and better resistance to nucleophilic substitution reactions.(Nemanick, Hurley et al. 2006; Amy,
Michalak et al. 2007) Although organic functionalization presents better properties relative to hydride or oxide termination, the techniques to achieve such terminal groups typically employ either oxide or hydride terminated silicon as the precursor surface. Particularly, hydride surfaces control the chemistry and uniformity of the organic monolayers that anchor to the silicon surface via surface deprotonation and silyl radical formation. (Robins, Stewart et al. 1999) Crystal orientation also plays a crucial role in organic monolayer packing due to difference in atomic density and valency of activated surface silyl species with orientation. For example, a dihydride terminated (100) silicon surface allows two organic molecules per each surface silicon, while a monohydride terminated (111) surface allows one organic molecule per surface silicon.

1.3 Indirect Si-O-Si-R Functionalization

Indirect siloxane functionalization was first introduced as an alternative to physical adsorption of Langmuir-Blodgett layers on metal/semiconductor surfaces for dielectric applications. Siloxanes are especially beneficial for instantaneous passivation of exposed surfaces during any conformational changes besides offering a variety of surface functional groups for various applications. Typical applications of silanes include wetting, adhesion, lubrication and high-precision nanolithography. (Kluth, Sung et al. 1997) The siloxane condensation reactions are well documented with a similar mechanism as that of thiols condensation on non-reactive metal surfaces. (Dunaway and McCarley 1994) Spontaneous condensation reactions of self-assembling molecules result in chemically adhered monolayers such as thiols anchored on gold surfaces, carboxylic acids on carbonaceous surfaces and organosilanes ($R^2$-O-Si-$R^1$) yielding self-assembled siloxane (Si-O-Si-$R^1$) monolayers on silicon surfaces. Partially oxidized silicon surfaces
with hydroxyl (–OH) termination are preferred for silane self-assembly as the siloxanes are chemically reactive with hydroxyl terminated silicon, as per the equation 1.3.(Koelling and Kolb 1965)

\[
\text{Si-OH} + \text{R}^2\text{-O-Si-R}^1 \rightarrow \text{Si-O-Si-R}^1 + \text{R}^2\text{-OH}
\]

The reaction also yields an R²-OH by-product, which is usually volatile and may not affect the exposed silicon surface or the monolayer formed. The organosilane (R²-O-Si-R¹) precursors instantaneously react with hydroxyl terminated silicon surface to yield a 99% saturated Si-O-Si-R¹ monolayer within the first minute; however, a completely saturated siloxane monolayer on silicon is formed only after 24 h silane treatment. Instead of siloxanes, trichlorosilanes may also be used for instantaneous surface adsorption on silicon. Presence of trace moisture is beneficial for silane surface reactions as the moisture promotes hydroxyl termination on silicon, while excess moisture may promote polymerization of organosilanes resulting in a multilayer.(Kluth, Sung et al. 1997) Silane precursors are usually applied to hydride-terminated surfaces rather than native oxide terminated surfaces to obtain uniform monolayers. Notable disadvantages of siloxane functionalization may be inability to withstand HF etch due to underlying sub-oxides, which further hinders electronic and ionic transport to the underlying semi conductive silicon substrate for specific applications such as biosensors. Apart from conventional applications, siloxane precursors are recently applied as electrolyte additives for secondary lithium batteries to improve the capacity retention with charge/discharge cycling. The siloxanes are believed to alter the chemistry of the surface species, formed due to dissociation of the electrolyte;(Ryu, Lee et al. 2008; Song and
(Baek 2009) however, the affects of alcohol by-product upon desired chemistry of such surface species are unknown.

1.4 Direct Si-R Functionalization

Relative to indirect Si-O-Si-R monolayers, direct Si-R monolayers are anchored to the silicon substrate via a stable Si-C bond, which offers kinetic stability and less bond polarity. (Nemanick, Hurley et al. 2006; Amy, Michalak et al. 2007) Unsaturated or reactive precursors and silicon surfaces are activated via chemical, (Schmeltzer, Porter et al. 2002) thermochemical, (Teyssot, Fidelis et al. 2002) photochemical (Faucheux, Gouget-Laemmel et al. 2006) or electrochemical (Robins, Stewart et al. 1999; Koiry, Aswal et al. 2007) pathways (Stewart and Buriak 2002; Shirahata, Hozumi et al. 2005) to create silyl radicals, which in turn react with the activated precursors resulting in Si-R monolayer formation. Chemical techniques involve saturated, unsaturated or reactive precursors with Lewis acid or diacyl peroxide catalysts to accelerate silicon surface activation. (Buriak, Stewart et al. 1999) Thermal routes proceed via application of heat energy to silicon surfaces in order to reduce the activation energy barrier for Si-C bond formation. (Linford, Fenter et al. 1995) Silicon surfaces in unsaturated alkene or alkyne precursors may be heated at 200 °C to create a direct Si-R monolayer on the surface. The grafting temperature may be brought down to 50 °C using a diacyl peroxide catalyst in a thermo-chemical process. (Linford, Fenter et al. 1995) Lewis et al. (Bansal, Li et al. 1996) demonstrated a two-step halogenation/alkylation procedure to obtain halide/alkyl monolayers on silicon surfaces. In the first step, silicon surfaces are heated at 80 °C for 40 min in a saturated phosphorous pentachloride solution in the presence of a benzoyl peroxide catalyst to obtain a halide-terminated monolayer. In the second step, the halide
surfaces are heated in alkyl Grignard solutions at 95 °C for time periods ranging from 30 min – 24 h to obtain the alkyl termination. X-ray photoelectron spectroscopy characterization by Lewis et al. confirmed the intermediate halogenation and final alkylation of silicon surfaces. As thermal techniques provide excess energy to activate silicon surface and precursor molecules, control over uniformity of monolayer formation is compromised. Although thermally grafted monolayers show non-uniform monolayers due to dissociating surface layers, the technique is useful for functionalizing silicon nanoparticles or nanowires. Photochemical techniques activate silicon surfaces via deprotonation of hydride-terminated silicon using uv or white lights.(Faucheux, Gouget-Laemmel et al. 2006) Subsequently any unsaturated precursor with acidic hydride may be chemically attracted by the reactive silyl species to create an anchoring Si-C bond. Photosensitive organic precursors are used for this technique, where photo-activated precursor radicals deprotonate the silicon surface and form the monolayer. The technique provides an alternative to thermal route, but lacks the relative ease and control of applied surface energy due to intricate problems in maintaining uniform light intensity throughout the surface. Electrochemical routes offer the ease and precise control over the surface charge uptake relative to other pathways.

1.5 Electrochemical Grafting

Electrochemical routes typically include cathodic reduction of unsaturated (alkenes/ alkynes/ aromatic) molecules, organohalides or diazonium salts and anodic oxidation and subsequent grafting of reactive molecules such as alkyl Grignards onto silicon surfaces. Cathodic electrografting mechanism is previously reported to proceed via silyl radical formation on porous silicon surfaces.(Robins, Stewart et al. 1999)
Cathodic potentials deprotonate the acidic hydrides from unsaturated precursor, while the precursors extract hydride from silicon surface to create a silyl radical. The silyl radicals would then react with another deprotonated organic precursor to create the Si-C bond and subsequently a monolayer. Cathodic reduction of organohalides on porous silicon surfaces is also reported to follow a similar mechanism as reduction of unsaturated precursors. (Gurtner, Wun et al. 1999) Robins et al. (Robins, Stewart et al. 1999) demonstrated both anodic and cathodic electrografting of phenylacetylene on porous silicon surfaces via chronopotentiometry technique; however, the cathodic reduction potentials are not presented. Fidelis (Fidelis, Ozanam et al. 2000) demonstrated formation of alkyl monolayers on silicon via anodic electrochemical grafting. Lewis et al. (Nemanick, Hurley et al. 2006) demonstrated electrochemical Grignard oxidation after reducing the Grignard solution first; however, redox reactions of tetrahydrofuran (THF) solvent may interfere with Grignard grafting on the surface. In this context, a detailed investigation is crucial to establish Grignard and THF redox potentials and the anodic grafting mechanism of Grignards on silicon surfaces. In this work, electrochemistry of short-chain alkyl Grignards and unsaturated organic precursors such as phenyl acetylene and 5-hexynoic acid are investigated to establish corresponding redox potentials and grafting mechanisms. The resulting organic monolayers with established grafting mechanisms may be further applied in the fields of microelectronics, gate dielectrics, biosensors, resists and functionalized silicon anodes for lithium batteries.

1.6 Overview

In this work, silicon surface functionalization with passive or reactive organic functional groups is demonstrated to address robust challenges in fields of gate
dielectrics, bio-immobilization, in situ patterned resists and silicon anodes for lithium batteries. In the first study (reported in chapter 2), passive alkyl monolayers are grafted onto (100) silicon surfaces via electrochemical or thermal oxidation of corresponding Grignard precursors. Grafted alkyl monolayers may be investigated for passivation performance against native oxide formation when exposed to ambient air. In the second study (reported in chapter 3), reactive 5-hexynoic acid and π–conjugated phenylacetylene monolayers may be obtained on crystalline silicon substrates via cathodic electrochemical reduction of respective precursors. In an earlier work, Scheibal(Scheibal, Xu et al. 2008) demonstrated cathodic grafting of 5-hexynoic acid on silicon nanowires (SiNWs) surfaces and further immobilized Bovine serum albumin (BSA) protein on the functionalized nanowires via 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) chemistry. In this study, cathodic monolayers are in situ patterned via dielectric microspheres and subsequently biotin or bovine serum albumin (BSA) immobilization on patterned 5-hexynoic acid monolayers is demonstrated for biosensor applications. Anodically grafted alkyl monolayers and cathodically grafted phenylacetylene monolayers maybe in situ patterned via dielectric PDMS stamps to obtain 1:1 inverse resists for patterned copper electrodeposition on silicon surfaces. Cathodic and anodic grafting mechanisms may be established for crystalline silicon surfaces based on cyclic voltammetry. Established grafting mechanisms may be further reinforced via chronoamperometry technique. Conventional surface characterization techniques such as Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) may be used to investigate the chemical quality of the monolayers. Novel characterization techniques such as atomic force microscopy (AFM) and electrochemical
impedance spectroscopy (EIS) are used to investigate the surface topography and conductivity of the monolayers respectively. The established grafting mechanisms may be further used to functionalize SiNWs for application as anodes in lithium batteries.

In the third and final study (reported in chapters 4-6), the direct or indirect functionalization techniques and chemical or electrochemical activation pathways may be used to functionalize nanoscale silicon to improve the performance as anodes in lithium batteries. Silicon anode functionalization may improve anode desirable properties such as adhesion with the conductive matrix, improved ionic conduction, and electron transfer reactions; however, most battery researchers do not consider varying silicon surface chemistry to improve the capacity, as the focus is mainly upon varying anode structure to compensate 300% volume expansion during silicon charging. In this context, a detailed investigation of silicon surface functionalization effects upon anode performance is presented. Silicon anode surfaces are functionalized in situ and ex situ via direct or indirect organic groups and the variations in cycling performance, surface chemistry, mechanical and electrical properties of the surface species are correlated. Cycling performance may be investigated using cyclic voltammetry and chronopotentiometry techniques. Anode surface chemistry, mechanical and electrical properties may be investigated via FTIR, XPS, AFM and EIS techniques. Silicon functionalization may be used to investigate and subsequently inhibit various factors causing capacity fade for silicon anodes in lithium batteries and in the process, functionalization effects upon silicon anode lithiation are discussed in detail.
2. ELECTROCHEMICAL AND THERMAL GRAFTING OF ALKYL MONOLAYERS ONTO (100) SILICON SURFACES*

2.1 Introduction

Silicon wafers with (100) surface orientation are most commonly used in conventional microelectronics manufacturing (e.g. CMOS, NVM, DRAM) processes. Silicon wafers are typically passivated by a thermally grown oxide layer that may be replaced with a hydride termination using a hydrofluoric acid etch before the use. Alternative passivation methods such as organic monolayers or multilayers may reduce toxic hydrofluoric acid use and improve the silicon-dielectric interface quality. Further, a stable surface chemistry against oxidation may enable novel silicon applications such as biosensors or lithium battery anodes where silicon surfaces are in direct contact with biological, humid, or any oxidizing environments. Alkyl monolayers anchored via direct Si-C bonds may provide such stable terminal chemistry to the silicon surfaces. Lewis et al. (Nemanick, Hurley et al. 2006), previously reported direct alkyl monolayers on (111) silicon surfaces prevent native oxide formation for ~71 days when exposed to ambient atmosphere (21% oxygen). A two-step halogenation/alkylation reaction was used to achieve ~95% methyl coverage on (111) silicon via thermal treatment of halogenated silicon in methyl Grignard solution. Fellah et al. (Fellah, Boukherroub et al. 2004), also reported the same thermal technique to create a methyl monolayer on (100) silicon that prevents native-oxide formation for ~30 days. Relatively short protection periods for (100) surfaces may be due to different packing densities of alkyl monolayers on (100) and (111) silicon surfaces. Electrochemical techniques to attach alkyl monolayers on silicon may improve the passivation performance of silicon surfaces due to precise

control over applied surface energy relative to the two-step halogenation/alkylation

Electrochemical routes to direct silicon surface functionalization include cathodic
electrografting of unsaturated diazonium salts (Allongue, de Villeneuve et al. 2003) or
alkynes (Robins, Stewart et al. 1999) and anodic electrografting of reactive
molecules (Fidelis, Ozanam et al. 2000) such as Grignard reagents. Grignards are
particularly interesting showing both thermal (Fellah, Boukherroub et al. 2004) and
electrochemical (Fidelis, Ozanam et al. 2000) activation pathways to achieve a silicon-
alkyl termination via a direct Si-C bond. Previous works with thermal passivation of
(111) silicon surfaces by methyl Grignards have shown >90% surface coverage; however,
the process is relatively slow (ranging from 3 hours (Yu, Webb et al. 2005) to 8
days (Bansal, Li et al. 1996)) and may not fully prevent oxidation of polycrystalline or
single crystal silicon (100) surfaces. Electrografting of methyl Grignards onto silicon
(111) surfaces have also been shown as an efficient route to achieve fully methylated
surfaces (Fellah, Teyssot et al. 2002; Teyssot, Fidelis et al. 2002). Chazalviel et al.,
previously established anodic grafting route to attach methyl groups on silicon surfaces,
but the technique was later criticized, claiming that the observed grafting is due to
tetrahydrofuran (THF) solvent oxidation and not Grignard. Lewis et al., showed that
Grignards may be oxidized only after cathodically reducing them first and provided a
mechanism based on the principle; however, cathodically reducing Grignards first, may
saturate the silicon surface with by-products due to THF redox reactions. In this work,
Grignard electrochemistry is clearly established and the effectiveness of (100) silicon
surface alkylation via thermal and electrochemical activation techniques is investigated. Further, the thermal and anodic electrochemical grafting mechanisms were discussed in detail. Figure 2.1 shows a schematic of alkyl monolayers grafted on (100) silicon surfaces via electrochemical or thermal activation routes.

Figure 2.1 Alkyl passivation of hydride-terminated (100) silicon surfaces via [A] electrografting; [B] thermal grafting.

2.2 Experimental

Anhydrous reagents including tetrahydrofuran (THF, 99%), 3M methyl and 2M ethyl Grignards in THF, hydrofluoric acid (HF, 48% ACS reagent), phosphorous pentachloride (reagent grade, 95%), benzoyl chloride (reagentplus, 99%) and benzoyl peroxide (reagent grade, 97%) were obtained from Sigma-Aldrich (Milwaukee, WI). Buffered Oxide Etch (BOE, ammonium fluoride/hydrofluoric acid etching mixture 6:1) and ethanol were obtained from Fischer Scientific (Pittsburgh, PA). All experiments were performed using polished p-type silicon wafers, 100 mm diameter with (100) orientation and resistivity ranging from 1-5 Ω·cm.

Silicon wafers were cleaved into 2x2 cm² samples and immersed in BOE solutions for 30 seconds to yield an atomically flat silicon dihydride surface (Higashi, Chabal et al. 1990; Buriak 2002). This procedure was followed by DI water rinsing and nitrogen drying prior to each grafting experiment. Thermal grafting and electrografting experiments were carried out in an argon atmosphere dry box system maintained with
less than 1 ppm of water or oxygen. The thermal grafting process involved heating hydride-terminated samples in benzoyl chloride solutions saturated with phosphorous pentachloride in the presence of 100 mM benzoyl peroxide at 80 °C for 40 minutes. Samples were subsequently washed with THF and immersed in methyl or ethyl Grignard solutions and heated at 95 °C for 8 hours to obtain the corresponding methyl or ethyl termination.

Electrografting involved attaching the silicon sample to working electrode followed by immersion into the grafting electrolyte along with a platinum counter electrode and silver wire pseudo reference. Ohmic connections were created to the backside of the silicon wafer with a GaIn eutectic. All electrochemical measurements were made under quiescent conditions at 10 mV/s scan rate and included a supporting electrolyte of 100 mM lithium hexafluorophosphate unless mentioned otherwise. Voltammetric experiments were performed using a Princeton Applied Research potentiostat (Model 263A). Potentials were adjusted to Ag/AgCl reference by measuring the potential difference between the pseudo reference and Ag/AgCl reference electrode immediately after each experiment. Samples were removed from the dry box following grafting experiments, rinsed several times with acetone and DI water sonicated in ethanol for 5 minutes, then rinsed and dried prior to storage or analysis. Infrared spectra were acquired using a Nicolet (Thermo Scientific, Madison, WI) Model 380 FTIR with Attenuated Total Reflectance (Spectra-Tech ATR, Model 55-390) multi-bounce system including a ZnSe waveguide (8cm x 1cm x 0.3cm, with 45° beveled facets). The sample was pressed against the top of the waveguide, while 512 scans (2 cm⁻¹ resolution) were taken using a Deuterated Triglycine Sulfate (DTGS) detector. X-ray Photoelectron
Spectroscopy (XPS) data were collected on an Axis 165 photoelectron spectrometer (Kratos Analytical) with the collection chamber maintained at $1.5 \times 10^{-9}$ Torr. An incident beam of soft X-rays (160 keV) from an Al Kα source was injected at an incident angle of 90°. AFM images were acquired using an Agilent 5500 AFM/SPM system equipped with Picoscan v5.3.3 software. V-shaped non-conductive silicon nitride cantilevers (MSCT-AUNM, resonance frequency 120 kHz, spring constant 0.5 N/m) were obtained from Veeco (Portland, OR) and an ambient environment was used for contact mode imaging.

2.3 Results and Discussion

2.3.1 Voltammetric Behavior of (100) Silicon in Grignard Solutions

Cyclic voltammetry is used to analyze and establish the electrochemistry of Grignard reagents in THF solvent. A step-by-step procedure is incorporated, where the potential window of THF is first analyzed with platinum working electrode, followed by the potential window of Grignards in THF with platinum, yielding the electrochemistry of Grignards. The Grignard electrochemistry is then analyzed with silicon working electrode to establish any shift in redox potentials relative to platinum working electrode. The scans are obtained at 10 mV/s scan rate with a supporting electrolyte of 100 mM lithium hexafluorophosphate used with pure THF solutions, while no supporting electrolyte is added when Grignards are used in a quiescent electrolyte. Figure 2.2 shows the cyclic voltammograms for platinum in THF (Figure 2.2A), silicon in methyl Grignard (Figure 2.2B) and platinum in methyl Grignard electrolytes (Figure 2.2C). The potential window of THF with 100 mM lithium hexafluorophosphate using a platinum working electrode is shown in Figure 2.2A. Platinum in THF shows an oxidation onset potential at
~0.1 V (vs. Ag/AgCl) and a cathodic reduction onset at ~ -2.5 V (vs. Ag/AgCl) indicating a 2.1 V potential window. When methyl Grignard is added to THF (1 M), the reversible Mg$^{++}$/Mg couple is observed at approximately -1.9 V (vs. Ag/AgCl) and the irreversible oxidation of the Grignard reagent is observed with an onset potential of approximately -400 mV (vs. Ag/AgCl) in Figure 2.2C. When the platinum working electrode is replaced with a hydride-terminated (100) silicon sample, the Mg reduction is consistent with the reduction potential on platinum (-1.9 V vs. Ag/AgCl); however, the oxidation potential is less abrupt and shifted positively by 500 mV to -1.4 V (Ag/AgCl) (Figure 2.2B). The shift represents oxidation of methyl Grignard occurs without significant oxidation of THF over a potential range of approximately 500 mV. Likewise, onset potential for methyl Grignard oxidation is shifted positively by approximately 300 mV on hydride terminated silicon surfaces relative to platinum working electrodes.

Figure 2.2 Cyclic voltammograms of [A] platinum working electrode in THF [B] (100) Si-H working electrode in methyl Grignard reagent (3 M in THF) [C] platinum working electrode in methyl Grignard reagent (1 M in THF).
Based on the results from Figure 2.2, potential window of -0.4 to 0.1 V (vs. Ag/AgCl) may be obtained for methyl Grignard electrografting on hydride terminated, p-type (100) silicon surfaces without oxidizing or grafting THF solvent. The electrochemical behavior of methyl and ethyl Grignards at (100) silicon electrodes was investigated within the stable anodic potential range from -1.4 V to 0.1 V (vs. Ag/AgCl). As shown in the voltammograms in Figures 2.3A and 2.3B, methyl Grignard oxidation on (100) silicon occurs at an onset potential of approximately -0.3 V (vs. Ag/AgCl) and ethyl Grignard oxidation on silicon occurs at an onset potential of approximately -1.0 V (vs. Ag/AgCl).

Figure 2.3 Cyclic voltammograms of [A] 2 M methyl and [B] 2 M ethyl Grignard reagents anodically grafted onto hydride terminated (100) silicon wafers. No supporting electrolyte was used.

Similar to the anodic behavior of methyl Grignard/THF solutions on platinum, methyl Grignard oxidation onset potential on (100) silicon occurs approximately 400 mV more cathodic to THF oxidation. Likewise, the onset potential for ethyl Grignard oxidation is approximately 800 mV more cathodic relative to THF oxidation. Anodic voltammetric scans of hydride-terminated surfaces with initial potentials greater than -1.9
V (Ag/AgCl) (without Mg reduction), do not show significant anodic current densities until Grignard oxidation is observed. As shown in Figure 2.3A, the first scan in 2 M methyl Grignard solutions with an initial potential of -1.4 V (vs. Ag/AgCl) shows an oxidation current observed at -0.4 V (vs. Ag/AgCl). A current hysteresis is observed on the first and second cycles along with a positive shift in the onset oxidation of approximately 300 mV. This hysteresis and shift in the onset potential is related to the irreversible silicon surface reaction with oxidized methyl Grignard reagents and subsequent surface passivation. Similar behavior is observed for electrografting of ethyl Grignards onto (100) silicon in 2 M solutions. As shown in Figure 2.3 B, a similar current hysteresis is observed with ethyl Grignards and the onset potential for oxidation is shifted approximately 200 mV positively in subsequent scans suggesting electrode passivation due to alkyl grafting.

Although the voltammetric behavior of hydride terminated (100) silicon surfaces are similar in both methyl and ethyl Grignard solutions; the onset potential for ethyl Grignard solutions is shifted approximately 500 mV cathodically relative to methyl Grignard solutions. The shift in onset potential relative to ethyl Grignards may be related to specific oxidation potentials of these Grignard reagents (Goebel and Marvel 1933). As seen in the voltammetric scans shown in Figure 2.3, surface reactions with methyl or ethyl Grignards appear complete after the first several scans and subsequent anodic scans show significantly diminished hystereses without any shifts in the onset potential.

It is also interesting to note that the oxidation of Grignard reagents continues after the surface reaction with silicon is complete. As shown in the forward scan in Figure 2.4, oxidation currents are dependent on the Grignard concentration in THF. The current
density for the anodic oxidation of methyl Grignards on grafted electrodes is approximately 15 mA/cm² greater in the 3 M solutions relative to the 1 M solutions. This behavior suggests oxidation current is proportional to Grignard concentration and products from the Grignard oxidation do not interfere with the grafted monolayer. The result also shows that at a higher potential (>0.1 V, Ag/AgCl), Grignard oxidation and surface grafting would still occur, but with a minor side reaction of oxidized THF grafting to the surface.

Figure 2.4 Linear scans showing Grignard oxidation on (100) silicon surface with an electrografted methyl monolayer in 3 M and 1 M methyl Grignard reagents.

2.3.2 Fourier Transforms Infrared Spectroscopy Analysis

Ex situ FTIR spectra for methyl and ethyl terminated (100) silicon surfaces obtained via electrochemical and thermal grafting methods are shown in Figure 2.5. Infrared adsorption associated with carbon-carbon interactions were not detected for ethyl (or methyl) terminated surfaces although the C-C bond is presumed to be present in the ethyl-terminated sample. The similarity in methyl and ethyl terminations in the spectral
range from 2600 to 3150 cm\(^{-1}\) is believed to be due to the crystalline alkyl environment at the surface. (Bansal, Li et al. 1996) As reported by Porter et al. (Porter, Bright et al. 1987; Mengistu, Goel et al. 2006) in describing the infrared spectra of alkyl thiols on gold surfaces, the presence of the pair of peaks at 2916 cm\(^{-1}\) (\(v_a\) CH\(_2\)) and 2850 cm\(^{-1}\) (\(v_s\) CH\(_2\)) also observed here, suggests alkyl species are arranged in a crystalline structure. The shoulder at 2960 cm\(^{-1}\) is due to the asymmetric CH\(_3\) stretch and is present in all spectra. In comparing spectra from electrografted samples with spectra from thermally grafted samples, thermally grafted samples show relatively broad peaks at 2916 cm\(^{-1}\) and 2850 cm\(^{-1}\) whereas electrografted peaks are sharper. The broad spectra from thermal samples are similar to spectra from thermally grafted alkyl monolayers on (111) silicon surfaces with an adsorption range of 2853-2858 (\(v_s\) CH\(_2\)) and 2921-2931 (\(v_a\) CH\(_2\)) (Mengistu, Goel et al. 2006) suggesting the presence of additional methyl groups that are not arranged in crystalline structure.

Static contact angles for thermally and electrochemically grafted (100) silicon surfaces were measured after 1 and 7 days of ambient air exposure. Contact angles for the functionalized samples indicate the hydrophobic nature of alkyl termination. The hydride terminated surface showed a significant decrease in contact angle over seven days from 102° to 24° indicative of native oxide growth. Contact angles for grafted surfaces decreased slightly from ~90° after 1\(^{st}\) day to 75-79° over a seven day period and the surfaces effectively maintained their hydrophobic nature for more than 60 days. The FTIR and contact angle results together confirm the presence of hydrophobic alkyl groups on the functionalized (100) silicon surfaces.
Figure 2.5 Fourier transform infrared spectra of 2 M ethyl Grignard (EG) and 3 M methyl Grignard (MG) grafted onto hydride terminated (100) silicon surfaces.

2.3.3 X-ray Photoelectron Spectroscopy Analysis

Silicon 2p spectra were acquired over several weeks to evaluate the stability of passivated (100) silicon surfaces after exposure to ambient laboratory conditions (~20-22 °C, 50-75% relative humidity). Lewis et al. used a similar technique to evaluate methylated (111) silicon oxidation in ambient atmosphere by observing a rise in the oxygen-shifted peak at 103 eV in Si 2p spectra. As shown in the XPS spectra for (100) silicon in Figure 2.6 (not grafted), a central Si 2p peak is observed near 99 eV and a smaller oxygen-shifted Si 2p peak is centered at ~103 eV consistent with oxidized silicon. The central Si 2p peak at ~99 eV with native oxide termination is slightly shifted (~0.2 eV) towards a lower binding energy value for hydride termination. This shift may be indicative of a fractional decrease in silicon oxidation state with hydride termination.
For hydride-terminated sample, the Si-Oₓ peak (103 eV) intensity after 1-day exposure to ambient air is much lower than that of native oxide, but increases significantly after 15 days exposure, approaching mature native oxide spectra after approximately four weeks ambient exposure (post HF treatment). The oxidation of alkylated silicon samples via thermal and electrochemical grafting methods may be monitored in a similar way as hydride by observing the rise in oxygen-shifted Si 2p peak at 103 eV.

Figure 2.6 X-ray photoelectron spectra for Si 2p region of hydride terminated (100) silicon samples exposed for 1 and 15 days to ambient air along with native oxide terminated (100) silicon sample.

The Si 2p spectra for electrografted and thermally grafted (100) silicon are shown in Figure 2.7 along with reference spectra from a mature native oxide. Electrografted and thermally grafted samples were analyzed after 1, 15, 35, 45 and 55 days exposure to ambient conditions. X-ray photoelectron spectra taken within the first 30 days following grafting show little variations in all samples, except a minor shift in central Si 2p peak at
99 eV towards a lower binding energy value. The shift is indicative of a fractional reduction in the silicon oxidation state relative to native-oxide termination. After 35 days of exposure in air, a small shoulder at 102 eV (Si-O_x) appears in the thermally grafted samples (Figures 2.7A and 2.7B) indicating the formation of oxides similar to a 1-day old hydride terminated samples.

![Figure 2.7 X-ray photoelectron spectra of Si 2p region showing the passivation performance of [A] thermally grafted methyl [B] thermally grafted ethyl [C] electrografted methyl and [D] electrografted ethyl monolayers onto (100) silicon surface.](image)

Electrografted samples reveal the same Si-O_x shoulder at 102 eV only after 55 days of exposure in ambient conditions as depicted in Figures 2.7C and 2.7D. The alkyl-grafted surfaces have shown better resistance to oxidation in air relative to hydride termination. The XPS behavior also suggests electrografted monolayers provide a greater
resistance to oxidation in ambient conditions relative to the thermally grafted samples. Also, the Si 2p peaks for alkylated silicon do not rise as fast as that of hydride, as the oxidation kinetics is at a much a lower rate on alkylated samples, especially on electrografted samples. In comparing the methyl and ethyl terminations, similar passivation performance is observed (effective for 55 days) showing a greater dependence on the passivation method (electrochemical versus thermal) rather than termination chemistry. The small peak at 102.8 eV present in the electrografted ethyl spectra after 55 days aging (Figure 2.7D) may also be indicative of the greater level of oxidation compared with similarly prepared methyl surfaces. This may be due to better surface coverage with compact methyl molecules rather than ethyl molecules with inherent steric effects.

2.3.4 Atomic Force Microscopy Analysis

Atomic force microscopy is used to analyze the topography and texture of alkylated (100) silicon samples after five and ten weeks of exposure to ambient air. The time periods are chosen based on the XPS results, where only thermally grafted samples are oxidized after five weeks (35 days) and both thermal and electrochemically grafted surfaces are oxidized after ten weeks (70 days). Figure 2.8 shows the AFM topographs of alkylated (100) silicon surfaces aged for 35 days. AFM topographs of (100) silicon surfaces electrografted with methyl and ethyl Grignards aged for 35 days are shown in Figures 2.8A and 2.8C respectively. A typical monolayer can be claimed in the ethyl-terminated sample shown in Figure 2.8A, with the exception of a single small area of adsorbates in the 3.5 x 3.5 nm² image. The average $rms$ roughness measured for the electrografted surface is 0.229 nm. A methyl monolayer produced after anodic
electrografting is shown in Figure 2.8C and also indicates a homogenous surface. Although imaging artifacts are present in Figure 2.8C, the results are consistent with a single layer of methyl functionalization obtained via electrografting.

![AFM images of passivated (100) silicon surfaces. (A) ethyl anodic electrografting; (B) ethyl thermal grafting; (C) methyl anodic electrografting; (D) methyl thermal grafting.](image)

Figure 2.8 AFM images of passivated (100) silicon surfaces. [A] ethyl anodic electrografting; [B] ethyl thermal grafting; [C] methyl anodic electrografting; [D] methyl thermal grafting.

The AFM topography for the thermally grafted (ethyl and methyl) surfaces (Figures 2.8B & 2.8D) immediately after grafting and after a series of solvent rinses reveals relatively higher levels of roughness including the presence of interspersed protrusions. Although the theoretical dimensions for the upright methyl and ethyl terminations are 0.3 nm and 0.5 nm respectively, measured \( \text{rms} \) roughness for thermally grafted samples is typically greater than 10 nm. As shown in Figure 2.8B, \( \text{rms} \) surface roughness decreased from 10.74 nm to 0.72 nm after sonication in ethanol for 5 minutes.
(Figure 2.9A). The islands are speculated to be nanoscopic regions of oxides or suboxides or organic adsorbates including reaction byproducts formed during thermal treatment. The source of these adsorbates was investigated, by treating a glass slide in the methyl Grignard solution under similar conditions (3 M, 8 h at 95 °C) followed by AFM analysis. In this case adsorbates of similar morphology were detected by AFM analysis and remained attached to the glass slide after repeated rinsing and sonication.

Figure 2.9 AFM images of thermally grafted methyl monolayer. [A] topographs before HF dip and corresponding [B] friction before HF dip; [C] topographs after HF dip and corresponding [D] friction after HF treatment.

Thermally grafted samples such as those shown in Figure 2.9A with 0.72 nm \( \text{rms} \) roughness (measured after three sonication and rinse steps) were also treated with 10% HF for 5 seconds to evaluate native oxides as a potential origin of the elevated surface roughness. Figure 2.9 shows the AFM morphological difference before and after the HF dip. The triple contrast observed in Figure 2.9A, has been reduced to a double contrast
(Figure 2.9C), which is consistent with the dissolution of silicon oxides in HF. The change in contrast after an HF dip suggests strongly adsorbed species may remain on the surface that are neither stripped in HF nor detached during sonication. (Tsumura, Ando et al. 1998) The multiple contrasts in the friction images (Figures 2.9B & 2.9D) further indicate thermally treated samples are more heterogeneous and composed of an organic monolayer, silicon oxides and organic adsorbates. The AFM images shown in Figure 2.10 show a change in morphology before and after a 1 minute 10% HF dip of a 70-day old methyl-functionalized sample (grafted via electrochemical or thermal routes).

Figure 2.10 AFM topograph images of (100) silicon surfaces after 70 days electrografted with methyl; [A] before HF and [B] after HF treatment and thermally grafted with methyl; [C] before HF and [D] after HF treatment. (Vegunta, Ngunjiri et al. 2009)
Only slight morphological changes are observed for the electrografted sample including a decrease in measured \( \textit{rms} \) from 0.477 nm to 0.163 nm after the HF dip. This may be associated with dissolution of raised oxides that may have formed at defect sites. In contrast, the \( \textit{rms} \) surface roughness of thermally grafted surfaces (aged for 70 days) increased more than three-fold (1.46 nm before to 4.11 nm after) after HF treatment (Figures 2.10C & 2.10D). This behavior suggests a greater level of oxide formation, disorganized grafting, and the presence of oligomerized species adsorbed on thermally grafted samples. As shown in Figure 2.10, the adsorbed species appear to remain after HF treatment suggesting they are attached to the grafted layer rather than oxidized silicon. The AFM analysis clearly suggests thermal grafting technique provides excess energy to Grignards and silicon surface resulting in polymeric solution species depositing on the grafted surface as a side reaction.

2.3.5 Anodic Electrografting Mechanism

Anodic electrografting mechanism is proposed based on the cyclic voltammetry results observed in section 2.3.1. According to a mechanism proposed by Fellah et al. (Fellah, Teyssot et al. 2002; Teyssot, Fidelis et al. 2002) for anodic electrografting of alkyl Grignards on (111) silicon, the reaction proceeds via the oxidation of Grignard reagents resulting in the formation of alkyl radicals. In the subsequent electrochemical step, a hole reacts with surface hydrogen (Si-H) to form an active silyl species via deprotonation in a rate-determining step (RDS). An alkyl radical (R˙) abstracts hydrogen from the hydrogenated silicon surface. The activated surface (\( \equiv \text{Si}^- \)) is expected to be strongly reactive and alkyl grafting occurs according to the final reaction step. (Fellah, Teyssot et al. 2002; Teyssot, Fidelis et al. 2002)
This mechanism by Fellah et al. (equations 2.1-2.4) could not hold as the Grignard oxidation step was not validated. Lewis et al. further suggested the reaction proceeds via silyl species formation by cathodic reduction of Grignards and then oxidizing the Grignards later to attach the alkyl radicals onto the surface. This mechanism by Lewis et al. may not be true as only the cathodically reduced Grignards show oxidation peaks and no oxidation peaks were observed at the reported potentials without reduction first; however, Lewis et al., indeed suggested a difference in claimed Grignard oxidation potentials (which may be Grignard salts).

In section 2.3.1 of this study, Grignard electrochemistry and grafting on (100) silicon are clearly established. As seen in the voltammetry in Figure 2.3, the difference in onset potentials for ethyl and methyl electrografting on (100) silicon surfaces (approximately 600 mV), suggests the first step toward electrografting may involve oxidation of the Grignard reagent rather than the formation of a silyl species. In this case, Grignard oxidation yields an alkyl radical which abstracts hydrogen from the dihydride (100) surface. As suggested by Fellah et al. (Fellah, Teyssot et al. 2002; Teyssot, Fidelis et al. 2002), another alkyl radical may subsequently react with the activated silicon surface (=Si’) forming a covalent Si-C bond in the rate-limiting step. The rate-limiting step is chosen to be different from that of Fellah et al. as the reactive alkyl radicals almost instantaneously deprotonate the silicon hydride surface to create silyl radicals. The
variation of grafting potential with alkyl grafting further suggests that the alkyl grafting onto the surface silyl radicals may be the rate-limiting step. While complete methyl coverage of (111) surfaces may be possible, the distance between adjacent silicon atoms on (100) surfaces is approximately 4 Å and Density Functional Theory (DFT) calculations indicate that bond lengths of the Si-C and Si-H at an angle of 120° together constitute a length of approximately 3.5 Å. (Jing and Whitten 1992) Thus the first Si-C bond formed on the (100) surface sterically hinders grafting of a second alkyl group resulting in a 1:1 alkyl per surface silicon ratio. The schematic in Figure 2.11 shows the mechanism proposed for anodic electrografting on dihydride terminated (100) silicon surfaces. As shown in the proposed mechanism in Figure 2.11, the anodic reaction follows a two hole (or electron) per silicon process where both the holes participate in Grignard oxidation and the formation of alkyl radicals. In fact, this mechanism is in close agreement with charge estimates based on the charge hysteresis measurements shown in Figure 2.3. The charge difference between the forward and reverse scans on the first cycle shown in Figure 2.3 is 154 μC/cm² for methyl Grignard and 228 μC/cm² for ethyl Grignard. Although coulombic efficiency toward electrografting reactions is unknown, these charges are comparable to the theoretical values required for complete coverage of (100) silicon (217 μC/cm²) assuming two holes are required for each electrografting reaction and one alkyl group is covalently bonded to each surface (100) silicon atom.

As demonstrated here, anodic electrografting of Grignard reagents provides a direct hydride substitution process that proceeds through reactive alkyl radicals generated by the oxidative decomposition of the Grignard reagent. There is no need for an intermediate halide (i.e. Si-Cl) as suggested by Lewis et al. and the oxidation reaction is
well controlled to afford a homolytic dissociation of the Grignard molecule. \((\text{RMgX} \leftrightarrow \text{R}^* + \text{•MgX})\). In the rate-determining step, electrochemically-generated radicals abstract hydrogen from the surface Si-H bond (90 kcal/mol) and form a covalently bonded Si-C surface. The process appears to be self-limiting as the electrografting reaction tends to increase the potential required to reach the same level of Grignard oxidation once the initial passivation is complete. It is also interesting to compare electrochemical and thermal routes considering a similar Grignard oxidation mechanism is present in both the pathways although the resulting passivation behavior is quite different.

Figure 2.11 Schematic for the mechanism of anodic electrografting of alkyl Grignards on dihydride terminated (100) silicon surfaces.

2.3.6 Thermal Grafting Mechanism

As described by Lewis et al. (Nemanick, Hurley et al. 2006), thermal grafting procedures with Grignard solutions typically involve a chlorination pre-treatment step
followed by an alkylation step. Based on soft XPS results, a monochloride-terminated (100) silicon surface is obtained in an initial step with PCl$_5$ and chlorobenzene. (Nemanick, Hurley et al. 2006) The chloride termination is retained during treatment in THF alone but completely replaced with alkyl groups after exposure to alkyl Grignards at 95 °C temperature for 8 hours. The mechanism for the formation of a grafted monolayer on (100) silicon via this thermal route is proposed to be equivalent to the reaction on (111) surfaces. (Nemanick, Hurley et al. 2006) Silicon passivation proceeds through the simultaneous formation of a cationic silyl species and oxidation of the alkyl Grignard. Subsequent steps differ greatly from electrografting pathways due to the need of an impurity from the solution (i.e. RX, alkyl halide reduced during Grignard oxidation) to help reduce the build-up of an interfacial energetic barrier that hinders electron injection from solution to attach the alkyl radicals to silicon surface. (Nemanick, Hurley et al. 2006) In contrast with methylated (111) silicon surfaces created by thermal processes, the XPS results presented here indicate passivation performance is relatively weaker for (100) surfaces. In addition, thermally grafted samples show relatively lower levels of passivation performance compared to electrografted samples. The origin of the relatively lower level of passivation observed with thermally grafted samples may be due to reduced or incomplete chlorination of dihydride terminated silicon, incomplete alkylation of cathodic sites, or adsorbate shielding.

Steric limitations associated with (100) dihydride surface likely prevent complete chlorination (1:1 Si: Cl) as possible with monohydride (111) surfaces demonstrated by Lewis et al. (Nemanick, Hurley et al. 2006; Nemanick, Hurley et al. 2006) This partial chlorination may result in relatively lower surface alkyl coverage and decreased
passivation performance of (100) surfaces relative to (111) surfaces. Indeed, results from Lewis et al. show (111) surfaces thermally grafted with methyl Grignard are stable for approximately 70 days exposure in ambient conditions whereas thermally grafted (100) surfaces shown in this study are stable for approximately 30 days. The incomplete chlorination of (100) surfaces may lead to regions of silicon surface, which retain their dihydride termination after the thermal grafting step and are more prone to oxidation after the thermal grafting process.

Fellah et al. (Fellah, Boukherroub et al. 2004) suggest the thermal mechanism proceeds through formation of pools of anodic and cathodic sites in accordance with the partial chlorination of the surface. While anodic sites may undergo relatively fast alkylation, the non-chlorinated cathodic sites (with dihydride terminations) may react more slowly before complete alkylation. (Fellah, Teyssot et al. 2002) In addition to incomplete chlorination and incomplete conversion of cathodic sites on (100) silicon surfaces, AFM results from thermally grafted samples (and smooth glass treated in the same solutions) suggest oligomers formed during the thermal process may be strongly adsorbed to silicon surfaces and prevent complete alkylation. It is not clear if the adsorbed species preferentially affect chlorinated, non-chlorinated, anodic or cathodic areas or if the adsorption pattern is random.

The results presented here suggest thermal grafting mechanism also relies on Grignard oxidation and may not require a conductive surface. In contrast with thermal methods, electrografting methods allow the application of uniform anodic potentials across silicon surfaces and may also be used to control the rate of Grignard oxidation. As shown in the voltammetric experiments presented in Figures 2.3 and 2.4, Grignard
oxidation and surface alkylation is associated with hysteresis in initial scans and subsequent scans show increased electrode passivation without hysteresis. This passivation and shift in Grignard oxidation onset potentials results in a self-limiting electrochemical process and yields a continuous monolayer.

2.4 Conclusions

Silicon surfaces with (100) orientation were alkylated via thermal and electrochemical activation of corresponding Grignards. Cyclic voltammetry was used to establish a ~300 mV potential window for electrografting alkyl groups via Grignard oxidation on silicon without grafting THF. Voltammetric analysis during the electrografting process showed significant hysteresis in the first anodic scan of hydride-terminated (100) silicon in both methyl and ethyl Grignard solutions. Subsequent anodic scans shows the loss of current hysteresis and onset potentials are anodically shifted suggesting passivation of silicon surfaces. In comparison with alkyl grafting via thermal methods, electrografted samples show relatively sharper IR absorbance spectra and relatively smoother AFM topographs. Further, electrografted silicon surfaces show excellent stability relative to hydride-terminated and thermally grafted silicon surfaces and are effective at limiting native oxide formation for more than 55 days in ambient conditions. Differences in the oxidation behavior are attributed to incomplete alkyl coverage associated with the electroless nature of the thermal grafting or adsorbate shielding. A refined mechanism is proposed for anodic electrochemical grafting of Grignards on silicon surfaces based on the cyclic voltammetry results. The electrochemical grafting method demonstrates a facile route to functionalize silicon surfaces for various applications including novel microelectronics (viz. gate electrode)
processing methods, high-capacity lithium battery anodes and manufacturing novel organic-semiconductor interfaces. The established anodic grafting mechanism may offer alkyl termination for selective metal electrodeposition or silicon etching processes and further provide an opportunity to investigate the cycling behavior of functionalized silicon anodes to establish better reversibility and high-capacity for lithium batteries.
3. IN SITU ELECTROGRAFTED MONOLAYER PATTERNS ON (100) SILICON*

3.1 Introduction

Monolayer patterning allows precise spatial control of surface chemistry and fabrication of integrated silicon-organic devices such as molecular wires, molecular transistors, or biosensor arrays with excellent specificity. (Zeng, Wang et al. 2007) In this chapter, an in-situ electrochemical method is demonstrated for patterning direct organic monolayers onto silicon surfaces. The technique is an alternative to optical, electron beam or scanning probe-based monolayer patterning methods and is driven by an electrochemical potential in the presence of dielectric templates. The electrochemical potential may be anodic for oxidation of reactive molecules such as Grignards or cathodic for reduction of unsaturated alkenes, alkynes or diazonium salts. Anodic electrochemical grafting and characterization of alkyl monolayers on (100) silicon was demonstrated in the previous chapter. Cathodic grafting of unsaturated alkynes on (100) silicon had been a challenge, as the thermal or electrochemical attachment of alkynes on crystalline (100) silicon were previously unconfirmed. In this chapter, cathodic electrochemical grafting of unsaturated 5-hexynoic acid and phenyl acetylene monolayers on (100) silicon surfaces is demonstrated and the mechanism is reinforced via electrochemical techniques.

Silicon surfaces may be patterned via indirect siloxane (Si-O-Si-R) or direct (Si-R) monolayers. Indirect siloxane monolayer patterning has been demonstrated using several techniques including: photolithography(Sun, Chong et al. 2005), e-beam lithography(Lercel, Craighead et al. 1996), and several scanning probe based techniques(Sugimura and Nakagiri 1997; Maoz, Frydman et al. 2000; Maoz, Frydman et

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al. 2000; Hurley, Ribbe et al. 2003; Zhang, Balaur et al. 2006) including: Dip Pen Nanolithography (DPN)(Sugimura and Nakagiri 1997; Hurley, Ribbe et al. 2003), nanoshaving(Zhang, Balaur et al. 2006) and constructive nanolithography(Maoz, Frydman et al. 2000; Maoz, Frydman et al. 2000). These scanning probe methods may be used to create monolayer features on silicon as small as 20 nm; however, the serial (scanning) process is relatively slow and not suitable for large areas. Aswal et al.(Aswal, Koiry et al. 2009) first demonstrated an electrical method to pattern large areas of monolayers using a metal grid to oxidize (methyl-terminated) octadecyltrichlorosilane (ODTS) functionalized silicon surfaces. In this process, a large-area copper grid is pressed against ODTS-modified surface in air and an anodic bias of ~20 V is used to locally oxidize the methylated surface. (Aswal, Koiry et al. 2009) The technique allows patterning of larger areas (several cm$^2$) in a single step; however, the resolution and uniformity are limited by the high (breakdown) potentials required and relatively non-uniform oxides.

Direct \((\text{Si}–\text{R})\) monolayers may be patterned via light-induced hydrosilylation (Stewart and Buriak 1998) and electrochemical methods with conventional lithography or atomic force microscope (AFM) directed electrografting. Charlier et al.(Charlier, Baraton et al. 2005) demonstrated an ex situ electrografting technique to pattern silicon surfaces via localized doping. According to Charlier, heavily doped silicon regions \((10^{19} \text{ cm}^{-3}, \text{p-type})\) allow greater cathodic potentials and thicker oxide layers acting as ohmic resistors resulting in thinner grafted films than poorly doped silicon areas. Although local doping enables preferential electrografting of silicon surfaces, lithographic constraints and dopant diffusion limit the resolution to 300 µm and tendency of highly doped silicon to
oxidize more readily relative to undoped or intrinsic areas concern the technique. (Charlier, Baraton et al. 2005) Conductive scanning probe lithography using a Pt-coated AFM tip on hydride-terminated silicon can be used to inscribe spatially defined arrays of alkyl termination. (Hurley, Ribbe et al. 2003) Unlike other electrografting techniques, the close proximity of the AFM tip to the hydride-terminated silicon surfaces enables highly localized electrochemical reaction with lines as thin as 40 nm have been achieved. However, the AFM writing process is serialized and substantially slow, requiring thousands of tips to create patterns over millimeter areas relevant to device manufacture.

In this chapter, a novel patterning technique is introduced where dielectric templates such as polystyrene (PS) microspheres and poly(dimethylsiloxane) (PDMS) stamps are placed in proximity to or in contact with silicon surfaces to channel the electrochemical potentials applied for grafting. Microsphere lithography is a low cost, high throughput process obtaining well-ordered periodic nanostructured arrays of various materials. (Haynes and Van Duyne 2001) The self-assembly of mono-disperse polystyrene spheres has been used to fabricate structures such as nanowires (Fan, Werner et al. 2006) and nanopillars. (Kuo, Shiu et al. 2003; Cheung, Nikolic et al. 2006) While electrografting reactions are dependent on the potential and electrolyte, the pattern shapes and dimensions are controlled by the microsphere properties e.g., size, permittivity and the self-assembly behavior. The process allows patterning of large areas and the resulting 5-hexynoic acid films may be used for selective protein immobilization. (Scheibal, Xu et al. 2008) Patterned PDMS templates are physically pressed against the silicon to block the electrolyte contact with the template-covered areas, limiting the grafting reactions to
the exposed surface. The PDMS templates may provide micron-scale patterns and allow both anodic and cathodic grafting of monolayers on silicon surfaces. Passive phenyl acetylene or methyl films patterned via PDMS stamps may be used for selective deposition processes such as atomic layer deposition (ALD) (Chen, Kim et al. 2004), electrodeposition (Zhang, Balaur et al. 2006), or the chemical etching process (Sugimura, Nakagiri et al. 1995).

3.2 Experimental

Single-side polished (100) silicon wafers (100 mm diameter, p-type, 1–5 Ω•cm resistivity) were obtained from Montco. 5-hexynoic acid, phenyl acetylene, tetraethyl ammonium perchlorate, copper (II) sulfate pentahydrate, 3 M methyl magnesium chloride (methyl Grignard) in tetrahydrofuran (THF), nitric acid, sulphuric acid and hydrofluoric acid (HF) were obtained from Sigma-Aldrich. Approximately 1-2 cm² samples were cut from (100) oriented silicon wafers. Oxides were stripped using a buffered oxide etch with dilute HF via immersion for 10 s. Samples were rinsed with DI water and immediately used for template deposition and subsequent electrografting processes.

3.2.1 Template Deposition

PS microspheres (1 μm diameter, ε = 2.5, 1% solid content) were obtained from Duke Scientific, as a suspension in water. Further, concentration of spheres was performed by removing 50% of the water in the suspension via centrifuging. 50 μL solutions of PS spheres were deposited on the hydrogen-terminated silicon substrates and stored in Teflon containers to dry for three days in ambient conditions. The samples were immersed in buffered oxide etch for 5 s and dried before being transferred into the dry-box, Vacuum Atmosphere, Hawthorne, CA. PDMS stamps were prepared in-house for
microchannel templates using a 10:1 (w:w) mixture of SYLGARD (Dow Corning) silicone elastomer and curing agent. After curing, thin and parallel stripes were carved from the pads using a sharp razor to form micron-size (~100-500 μm) channels. Stamps were pressed against hydride terminated silicon surfaces prior to immersion in grafting electrolytes.

3.2.2 Electrografting

Electrografting experiments were performed in a typical electrochemical cell using silicon working electrode, a silver wire pseudo reference electrode, and a platinum wire counter electrode, attached to a PAR 263A potentiostat, Oak Ridge, TN. Silver wire pseudo reference potentials were adjusted to Ag/AgCl by measurement after each experiment. Electrografting experiments were performed via cyclic voltammetry in phenyl acetylene or 5-hexynoic acid solutions or chronoamperometry in methyl Grignard and phenylacetylene solutions. A supporting electrolyte of 100 mM tetraethyl ammonium perchlorate was used with phenyl acetylene and 5-hexynoic acid solutions. Following electrografting experiments, silicon samples were rinsed thoroughly with ethanol and DI water and sonicated to remove the microspheres and other adsorbates. Cyclic voltammetry was used to establish the electrochemistry and potential windows for cathodic grafting of phenyl acetylene and 5-hexynoic acid precursors. In the potentiostatic mode, phenyl acetylene monolayers were cathodically electrografted on hydride terminated silicon surface at a constant potential of -1.5 V (versus Ag/AgCl) (Ngunjiri, Vegunta et al. 2009) for 120 s. Anodic methylation of (100) silicon was performed in the same experimental cell, at a constant potential of +0.1 V (versus Ag/AgCl) (Vegunta, Ngunjiri et al. 2009) for 120 s in 3 M methyl magnesium chloride in
THF without any supporting electrolyte. Electrografted samples were removed from the cell, rinsed with DI water and sonicated in isopropanol (and toluene to remove polystyrene spheres) followed by drying. The grafted surfaces were further characterized using AFM and impedance analysis.

3.2.3 Characterization

Ex-situ AFM measurements were performed in ethanol with an Agilent 4500 AFM instrument operating in contact mode. Silicon nitride probes (Veeco Probes) with spring constants of 0.5 N/m were used for imaging and monolayer stripping experiments. Typical imaging forces ranged between 0.1 and 5 nN, stripping forces of 8 nN were applied with T type cantilever. The carboxylic-acid-terminated surface derived from electrografting 5-hexynoic acid was converted to an activated ester via reacting with 1-ethyl-3,3-dimethylaminopropyl carbodiimide (EDC), Pierce Biotechnology, Rockford, IL and then coupled to amine groups of the proteins through amidization. Electrografted substrates were immersed in a solution of 0.2 mM EDC for 30 min. followed by incubation in a 0.1 µL/mL of biotin, BioAssay Works, Ijamsville, MD for 30 min. The patterned surfaces were characterized using an Agilent 5500 AFM/SPM (scanning probe microscope) system operating in contact mode, with Picoscan v5.3.3 software. Oxide-sharpened Si₃N₄ probes of $k_{avg}= 0.5$ N/m NPS from Veeco Probes, Santa Barbara, CA were used for imaging in air. The reported AFM images were collected in the constant force mode with the applied forces ranging between 1 and 10 nN. Substrates with PDMS-patterned methyl or phenyl acetylene monolayers were copper electroplated (10 mA/cm² for 40 s) in a 0.1 M CuSO₄ and 0.5 M H₂SO₄ electrolyte. Impedance analysis was performed in the same electrolyte (0.1 M CuSO₄ + 0.5 M H₂SO₄) with alternating current
(AC) amplitude of 10 μA (rms value) and no direct current (DC) bias in the frequency range of 10 mHz to 2 MHz.

3.3 Results and Discussion

3.3.1 Template Deposition

Organic monolayer patterns may be created on silicon surfaces using either anodic or cathodic processes with proximal or direct placement of dielectric templates.

Figure 3.1 Electrografted patterns via A. multi-layered polystyrene microspheres and B. PDMS stamp with microchannels. (Vegunta, Ngunjiri et al. 2010)

Figure 3.1A shows a schematic of electrografted monolayers in patterns of hexagonal close pack (hcp) arrays created via proximal placement of polystyrene microspheres in a multi-layer. Self-assembled polystyrene spheres may be arranged in single, double or multilayers depending on the size, concentration and deposition of spheres on the substrate. (Hulteen, Treichel et al. 1999; Barros, Hisano et al. 2005; Wu, Peng et al. 2005; Ngunjiri, Vegunta et al. 2009) Previous work with silicon and polystyrene microspheres of 1 μm diameter (diluted to 0.5% by weight in solution)
primarily show double-layer stacking. (Ngunjiri, Vegunta et al. 2009) The silicon samples along with multilayer polystyrene templates were dipped in HF to renew hydride termination followed by immersion in the grafting electrolyte and attached to the working electrode. Grafting reactions were performed via cyclic voltammetry or chronoamperometry for 120 s. This proximal masking process with microspheres results in hcp arrays of monolayer islands after the polystyrene spheres are removed. Similarly, Figure 3.1B shows a schematic of PDMS (ε = 2.3-2.8) stamp placed in direct contact with hydride-terminated (100) silicon surfaces. In this case, surfaces in contact with the electrolyte undergo electrografting reactions and obscured surfaces remain hydride terminated.

3.3.2 Cyclic Voltammetry

Cyclic voltammetry was used to establish the cathodic electrografting potential windows for phenyl acetylene and 5-hexynoic acid. (Robins, Stewart et al. 1999) Figure 3.2 shows the voltammograms for phenyl acetylene (Figure 3.2A) and 5-hexynoic acid (Figure 3.2B) cycled four times within the potential range of 0.1 to -1.0 V (vs. Ag/AgCl). Phenyl acetylene shows cathodic reduction current density at approximately -0.5 V (vs. Ag/AgCl) while 5-hexynoic acid shows the same at -0.65 V (vs. Ag/AgCl). A hysteresis was observed on both phenyl acetylene and 5-hexynoic acid voltammograms in the first cycle, which tends to decrease with each subsequent scan. This declined hysteresis may be due to completed or saturated electrode passivation reactions with each cycle of electrografting corresponding monolayers. The coulombic charge densities for the first two cycles are 549 and 307 μC/cm², respectively, for phenyl acetylene and 160 and 90 μC/cm², respectively, for 5-hexynoic acid. Phenyl acetylene shows greater cathodic
current density, hysteresis and a more cathodic shift of grafting potential relative to 5-hexynoic acid, suggesting more effective passivation with electron-rich phenyl group offering steric effects towards grafting reactions.

Figure 3.2 Cyclic voltammetry plots for cathodic electrochemical grafting of alkynes on silicon (100) surfaces; A. Phenylacetylene and B. 5-hexynoic acid. Scan rate = 30 mV/s. (Ngunjiri, Vegunta et al. 2009)

Cathodic electrografting of phenyl acetylene or 5-hexynoic acid follows a similar mechanism as suggested by Robins et al. to electrograft phenyl acetylene on (111) porous silicon surfaces. As Robin et al. suggested, the unsaturated precursor molecules lose an acidic proton in an electrochemical step and the precursor radicals attack the silicon surface to form silyl radical species on the surface. The reactive silyl species further react
with another precursor radical to create a stable Si-C anchorage of the unsaturated molecule on the surface. The cyclic voltammetry results in Figure 3.2 show a difference in cathodic reduction potentials of phenyl acetylene and 5-hexynoic acid. The difference in potentials is due to different energy requirements for deprotonation of precursors, reinforcing the first step of the mechanism involves deprotonation of unsaturated precursor molecules. Furthermore, steric limitations may prevent the attack of carbanions across the (100) back bonds as proposed in the (111) silyl mechanism by Robins et al. Also due to steric limitations, saturation in the (100) surfaces is limited to a single electrografted group per silicon with a free hydride bond as shown in Figure 3.3.

\[
\text{H}_2\text{C}≡\text{C}^-\text{R}_2 + \text{e}^- \rightarrow \text{H} + \text{C}≡\text{C}^-\text{R}_2
\]

Figure 3.3 Possible reaction mechanism for the CEG of alkynes on silicon (100). Cathodic reduction of alkyne molecules to form the active carbanion, which initiates the reaction. (Ngunjiri, Vegunta et al. 2009)

Although cyclic voltammetry results reinforce the mechanism is similar to that proposed by Robins et al. with a single-electron transfer process, the cathodic charges observed here are significantly greater than expected. The estimated charges for electrografting based on areas under voltammograms are approximately 2.24 electrons per silicon and 0.65 electrons per silicon for 5-hexynoic acid and phenyl acetylene respectively, suggesting poor columbic efficiencies toward electrografting reactions or incomplete monolayers. Low columbic efficiencies are expected as most
electrochemically generated carbanions may not participate in the electrografting reactions. Also, steric hindrances may prevent the formation of complete monolayers i.e., one electrografted molecule per (100) silicon surface atom as shown in Figure 3.3.

3.3.3 Chronoamperometry

Chronoamperometry was used to obtain cathodically grafted phenyl acetylene and anodically grafted methyl monolayers on (100) silicon surfaces without any dielectric templates. Scheibal et al., previously demonstrated chronoamperometry of 5-hexynoic acid on silicon wafers and nanowires. Figure 3.4 shows the resulting chronoamperograms for cathodic grafting of phenyl acetylene (Figure 3.4A) and anodic grafting of methyl Grignard (Figure 3.4B) precursors for 120 s at corresponding grafting potentials obtained from respective cyclic voltammetry results. As shown in Figures 3.4A and 3.4B, the current density decreases in a roughly exponential fashion for both anodic and cathodic grafting, suggesting saturated monolayer formation and electrode passivation. The exponential decrease in current density with time may be due to a rapid formation of precursor radicals, which are immediately adsorbed onto the double layer capacitance of the (100) silicon electrode, subsequently forming a monolayer via surface Si-C bonds. Similar passivation behavior is observed when dielectric templates are used on silicon surfaces. Experimental charge densities were determined for these unpatterned methyl and phenyl acetylene monolayers and compared with theoretical charges for saturated monolayers. Charges were estimated (Figures 3.4A and 3.4B) via numerical integration and any background charges (due to steady state oxidation/reduction of the electrolyte) were subtracted to yield charge densities of 101 µC/cm² for phenyl acetylene and 256 µC/cm² for methyl monolayers. The differences in charge requirements and current decay
are related to cathodic and anodic grafting mechanisms. Cathodic processes are believed to proceed via formation of reactive silyl anions on the surface. As described by Robins et al. (Robins, Stewart et al. 1999), silyl anions are created by the reduction of (100) Si-H species, which further undergo nucleophilic attack by the unsaturated alkyl carbanions to yield a monolayer. This mechanism suggests one electron is required for each organic molecule covalently attached to the silicon surface and agrees with the experimental results from this work (101 μC/cm² versus a theoretical value of 108 μC/cm² for (100) silicon surfaces) suggesting nearly saturated (1 grafted molecule: 1 Si atom) phenyl acetylene monolayers.

Figure 3.4 Chronoamperograms for A. cathodic grafting of phenylacetylene at -1.5 V (vs. Ag/AgCl) with 0.1 M tetraethyl ammonium perchlorate supporting electrolyte and B. anodic grafting of methyl Grignard at +0.1 V (vs. Ag/AgCl) without any supporting electrolyte on (100) silicon. (Vegunta, Ngunjiri et al. 2010)
Anodic processes are considered to proceed via oxidation of reactive alkyl Grignards in solution to produce alkyl radicals. As described in a previous work (Vegunta, Ngunjiri et al. 2009), the proposed mechanism for anodic grafting requires two electrons to electrochemically oxidize two alkyl Grignard molecules. The first alkyl radical chemically attacks Si-H surface bonds to strip hydrogen and form silyl radicals and the second alkyl radical reacts chemically with the silyl species to form covalently bound Si-R species. In this case, the experimental charge for anodic electrografting of methyl Grignard is 256 \( \mu \text{C/cm}^2 \), which is near the theoretical value (217 \( \mu \text{C/cm}^2 \)) for a two-electron process, also suggesting complete methylation (1 grafted molecule: 1 Si atom) of (100) silicon surface. As shown in Figure 3.4B, the initial grafting current (t <5s) decays exponentially; however, the grafting current from 5-120 s decreases more gradually relative to cathodic grafting (Figure 3.4A). The relatively slower current decay is likely due to slower kinetics associated with the chemical steps involved in anodic grafting. As described by Vegunta et al. (Vegunta, Ngunjiri et al. 2009), the electrochemical oxidation step (of Grignards) is fast relative to subsequent chemical steps: hydrogen abstraction from Si-H species and surface alkylation. As the results suggest, for both anodic and cathodic grafting processes, the oxidation or reduction of precursors and the adsorption of precursor radicals on the surface double layer occur in a fast step. While formation of silyl species and Si-C bond are also fast, formation of Si-C bond may be limiting due to delay in mass transfer of precursor ions to the surface making it the rate limiting step in both anodic and cathodic grafting mechanisms.
3.3.4 Microsphere Lithography and AFM Analysis

Silicon surfaces with polystyrene microspheres (1 μm in diameter) templates were cathodically electrografted with 5-hexynoic acid and phenyl acetylene to create nanoscale patterns and compared with unpatterned monolayer surfaces. Surface topography of patterned and unpatterned electrografted monolayers are analyzed via AFM imaging technique. Figure 3.5 shows the AFM topographs for 5-hexynoic acid monolayers.

Figure 3.5 AFM images of electrografted 5-hexynoic acid on (100) silicon; A. Unpatterned, B. and C. Nano-scale patterns D. Magnified view of a hexagonal close packing arrangement E. Individual cursor profiles measured and F. Histogram for measured heights of nanostructures for patterns in C. (Ngunjiri, Vegunta et al. 2009)
Figure 3.5A shows the unpatterned 5-hexynoic acid monolayer with ~0.4 nm rms roughness suggesting a densely packed, uniform film. Minute defects may be observed with darker contrast, associated with step edges (0.2 nm) or HF treatment resulting in a rough silicon surface. Figure 3.5B shows the AFM topograph of patterned 5-hexynoic acid monolayer islands of ~50-100 nm in diameter. The topograph is shown in a larger scan area of 6.5 x 6.5 µm² in Figure 3.5C relative to topograph in Figure 3.5B with a 4 x 4 µm² scan area. Figure 3.5D shows a magnified topograph image of hexagonal central packing of 5-hexynoic acid monolayer islands. Figure 3.5E shows the individual thickness profiles of monolayer islands shown in Figure 3.5C, measuring ~0.6 nm above the surface. Figure 3.5F shows the monolayer height distribution analysis for 283 monolayer islands measured to be in the range of 0.5-0.8 nm. The monolayer height distribution over the range 0.5-0.8 nm is well in accord with the theoretical height of an upright oriented 5-hexynoic acid molecule, 0.55 nm. Also, the measured interpattern distance of ~1 µm from magnified AFM image in Figure 3.5D is close to a hexagonal close packed (hcp) arrangement of the monolayer islands.

Figure 3.6A shows a square pattern (500x500 nm²) shaved in a uniform unpatterned phenylacetylene monolayer by sweeping the AFM tip over the selected area at a high load (~8 nN) in ethanol. At high forces, organic monolayers are removed by the tip.(Zhang, Balaur et al. 2006) The average film thickness determined from line profiles in Figure 3.6A is 0.6 nm, which corresponds to the theoretical height of a freestanding phenylacetylene molecule, 0.67 nm.(Tao, Qiao et al. 2003; Pluchery, Coustel et al. 2006) Figure 3.6B shows hcp patterns of phenylacetylene monolayer islands created using 1 µm diameter polystyrene spheres as templates in electrografting process. The bright contrast
of ~150 nm diameter monolayer islands is associated with surface protrusions of grafted phenylacetylene molecules. Disparities in island contrast in the AFM image in Figure 3.6B may be due to substrate roughness (0.14 nm) or disturbances from the (high force, 0.5 nN) contact mode rather than multilayers or incomplete grafting. Figure 3.6C shows a schematic of the hcp pattern formed by in situ patterned electrografting in void spaces of stacked polystyrene multilayers. (Ngunjiri, Vegunta et al. 2009) The measured heights of electrografted phenylacetylene and 5-hexynoic acid monolayers are almost same as the up-right oriented molecules, which suggests no silyl radical formation during grafting due to cleavage of (100) silicon back bonds.

Figure 3.6 AFM analysis of A. tip-shaven area of unpatterned phenylacetylene monolayer and corresponding line profile; B. Nanopatterns (hcp arrangement) of phenylacetylene islands and corresponding line profile; C. Top-down schematic of the hcp arrangement of microspheres. Spheres shown in lighter contrast are located in the bottom layer and those in dark contrast are located in the top layer. (Vegunta, Ngunjiri et al. 2010)

To verify the patterned islands are a result of electrografted functional groups rather than the oxides or solution adsorbates, the patterned phenylacetylene sample was immersed in a buffered oxide etch solution for 20 s and imaged with AFM. As shown in
Figures 3.7A and 3.7B, phenylacetylene nanostructures retained structural integrity even after fluoride treatment suggesting the islands are solely made of organic monolayers rather than oxides or solution adsorbates. The dielectric polystyrene microspheres may concentrate the electric field through the open voids in microsphere arrays to localize the grafting reactions.

Figure 3.7 Phenylacetylene nanostructures after treatment with HF: A. Large area and B. magnified views. (Ngunjiri, Vegunta et al. 2009)

Figure 3.8 shows a schematic for the deposition and grafting patterns with polystyrene microspheres self-assembled in monolayers or bilayers. Polystyrene spheres typically self-assemble into a hcp patterned monolayer exposing periodic hexagonal pattern of voids when deposited from low concentration solutions (Figures 3.8A and 3.8B). (Hulteen, Treichel et al. 1999). If the field is directed by a monolayer of microspheres, a hexagonal pattern as shown in Figure 3.8B is expected with almost triangular shaped islands. (Hulteen and Vanduyne 1995; Tan, Sow et al. 2005) From our results, the observed pattern and dimensions of electrografted islands show a hexagonal central packing pattern and not a hexagonal pattern. This suggests that a bilayer or multilayers of spheres may be responsible for the observed patterns similar to Figure
3.8C. Bilayer or multilayers of polystyrene spheres typically arise with higher sphere concentrations or relatively hydrophobic silicon hydride surfaces, due to insufficient spreading of the spheres. (Figure 3.8C). (Hulteen, Treichel et al. 1999)

Figure 3.8 Schematic of self-assembled polystyrene microspheres deposition patterns; A. Deposition around the sphere base of a monolayer, B. Deposition in the void spaces of the monolayer of spheres, and C. Deposition from a double-layer template of spheres. Insets show the SEM images taken after electrografting experiments without sonication. (Ngunjiri, Vegunta et al. 2009)

The polystyrene spheres assemble themselves in crystallographic domains due to capillary forces (Denkov, Velev et al. 1992) that may exceed thermal energy $kBT$ of the particles and cause the spheres to compress into a pseudo-hexagonal shape in the packing. (Kralchevsky and Nagayama 1994) From our results the obtained hcp patterned monolayer islands support the theory that a second layer occupy half the triple sites of the
first layer at the bottom as shown in the schematic in Figure 3.8C. A third layer may settle on top of the second layer, commensurate with the first layer and the stacking order of the first two layers may be repeated as \textit{ABABAB}.(Barros, Hisano et al. 2005) The multilayer stacking may result in decreased ionic diffusivity of the unsaturated organic precursors relative to monolayer or bilayer stacking. The greater number of closed voids in multilayers may offer more tortuous path in (111) direction with reduced electric field, increased infrared drop and greater charge screening.

Multilayer stacks and the enhancement of field strength along open columns may help explain the disparity in diameter of the circular electrografted islands of \(\sim150\) nm for phenyl acetylene with a total available void space of \(\sim600\) nm diameter. Cathodic electrografting with 5-hexynoic acid with similar experimental setup showed similar hcp arrays of grafted islands of approximately 250 nm in diameter.(Ngunjiri, Vegunta et al. 2009) These results may also suggest a direct relationship between grafted feature sizes and electrolyte conductivity; 317.5 \(\mu\)S/cm for phenylacetylene and 533.0 \(\mu\)S/cm for 5-hexynoic acid. This proximity effect was further evaluated by simulating electric fields used for grafting including electrodes with dielectric templates (Maxwell 2.0). Figure 3.9 shows simulated equipotential bands in phenylacetylene electrolytes near the triagonal void spaces indicated along the line segment shown in Figure 3.6C).

Greater cathodic potentials near the center of the void spaces lead to the formation of small round islands (\(\sim150\) nm diameter) rather than complete filling of the triagonal space (\(\sim600\) nm per side). The passivating nature of the monolayer itself also limits the island growth. Simulation results from show a linear relationship between island size and electrolyte conductivity up to approximately 1500 \(\mu\)S/cm where the entire triagonal space
is grafted with the monolayer. This behavior may be beneficial as feature sizes may be reduced beyond the limits of the template through careful control of the template and electrolyte resistivity.

![Image](image)

Figure 3.9 Potential gradients near silicon electrodes with dielectric microspheres along the cross-section taken from the vertical plane defined by line segment in Figure 3.6C. Gradients are simulated via Maxwell 2.0 software with electrolyte conductivity of 317 \( \mu \text{s/cm} \). Blue band shows \(<675 \text{ mV}\) and red band shows \(>975 \text{ mV}\) potentials while intermediate bands show 30 mV variation in potentials. (Vegunta, Ngunjiri et al. 2010)

### 3.3.5 Selective Protein Immobilization

Selective protein immobilization on carboxylic acid functionalized silicon surfaces is demonstrated. Biotin molecules are immobilized on patterned 5-hexynoic acid terminated silicon surfaces via EDC chemistry. Figure 3.10 shows the corresponding AFM topograph and a histogram for height distribution of biotin-immobilized carboxylic acid islands. Silicon surfaces with 5-hexynoic acid islands were treated in a solution of EDC and biotin protein for 30 minutes. As shown in Figure 3.10A, biotin molecules are bound to the islands on the surface, increasing the 5-hexynoic acid monolayer island
heights. More missing islands are observed from the patterns, which may be due to insufficient reaction time or non-uniform island heights. The height of the islands from the AFM image vary over a range of 5-25 nm in a Gaussian distribution (Figure 3.10B) as expected for uncontrolled protein layering. The measured heights correspond to stacking of 2–10 biotin molecules (Detitta, Edmonds et al. 1976; Hu, Tani et al. 2007) associated with crystal-directed assembly and solution agglomeration inherent of proteins.

Figure 3.10 Biotin immobilization on nanopatterned 5-hexynoic acid. A. AFM image of attached biotin. B. Histogram for nanostructures heights. (Ngunjiri, Vegunta et al. 2009)
3.3.6 Selective Copper Electrodeposition

Direct contact (PDMS) dielectric templates were used to create micro-patterns of 1:1 “negative” or inverse monolayer patterns on the silicon surface. Methyl (anodic) or phenylacetylene (cathodic) monolayer patterns created via PDMS stamps were used in copper electrodeposition experiments. Figure 3.11 demonstrates copper deposits selectively on hydride terminated regions rather than methylated or phenylacetylene terminated regions. This behavior is attributed to the absence of nucleation sites on methylated surfaces. Chen et al. (Chen, Kim et al. 2004) suggested a similar nucleation inhibition model is involved in the ALD of HfO$_2$/ZrO$_2$ on silicon surfaces with siloxane monolayers. The absence of copper deposition on functionalized surfaces also suggests the monolayers are continuous without major voids or pinhole-type defects.

Figure 3.11 Microphotograph of a patterned silicon sample with A. methylated or B. phenylacetylene terminated surfaces (darker regions) and copper deposits in unpatterned regions. (Vegunta, Ngunjiri et al. 2010)

3.3.7 Impedance Spectroscopy

Impedance analysis was performed using grafted and hydride terminated surfaces in the same electrolyte used for copper deposition. Figure 3.12 shows the impedance
spectra of three silicon samples with hydride, phenylacetylene and methyl monolayers.

Figure 3.12A shows an equivalent electric circuit (Einati, Mottel et al. 2009) of an organic monolayer on silicon surface immersed in an electrolyte. $R_s$ represents the solution resistance, $R_{ct}$ represents the charge transfer resistance (including resistive effects of mass transfer impedance); $C_{dl}$ represents the double layer capacitance and $Z_{electrode}$ is the impedance of semiconductor silicon surface with a resistive element $R_{si}$ and space charge capacitance $C_{sc}$. Grafted monolayers provide additional capacitive ($C_m$) and resistive ($R_m$) components that are considered absent for hydride terminated samples (treated as control samples).

The overall impedance as a function of frequency is shown in Figure 3.12B and the phase behavior is shown in Figure 3.12C. At low frequencies ($<10$ mHz), impedance
is purely resistive and is comprised of $R_s$, $R_{ct}$, $R_m$ and $R_{si}$ components. The DC resistance of phenylacetylene surfaces is approximately two orders of magnitude greater than hydride surfaces. Likewise, the DC resistance of methyl surfaces is approximately five orders of magnitude greater than hydride surfaces. Similar resistance trends are observed across the entire frequency range. It is also interesting to note the distinctive effects of monolayers on the double layer capacitance. (Fabre, Hauquier et al. 2009) From Figure 3.12C, the methylated surfaces show two distinct capacitive peaks (10 Hz and 10 kHz) suggesting a greater packing density (Nemanick, Hurley et al. 2006; Vegunta, Ngunjiri et al. 2009) relative to phenylacetylene surfaces with overlapped capacitive peaks (1 Hz and 500 Hz). The relatively high DC resistances and distinct capacitive components of grafted surfaces reinforce the passivation behavior and further confirm the high packing density and defect-free nature of covalently bound alkyl monolayers.

3.4 Conclusions

In situ electrochemical monolayer patterning is a versatile process and may be performed anodically or cathodically using either direct contact or proximal placement of dielectric templates (or masks). Anodic processes with alkyl Grignard reagents appear to follow a two-electron grafting mechanism and cathodic processes with alkynes appear to follow a one-electron grafting mechanism. Either method may be used to create large-areas of covalently bound monolayer patterns in a relatively fast process (<120s). Thickness measurements of the electrografted film correspond to the molecular dimension of the electrografted molecule, suggesting that the organic monolayers are upright oriented. Contact masks, such as PDMS stamps, result in a 1:1 “negative” or inverse pattern of monolayer deposition. Pattern grafting with proximal masks, such as
self-assembled polystyrene spheres, allows pattern reduction relative to template dimensions due to increased local electric fields near the electrode. Feature sizes resulting from the proximal masking method are a function of the mask (and electrode) geometry and electrolyte conductivity. Impedance analysis of silicon electrodes with complete monolayers indicates grafted films are continuous and relatively defect-free.

The in-situ patterning technique is quite flexible and allows silicon surfaces to be patterned with passivating or reactive functional groups. In one example, passivated surfaces serve as “monolayer masks” for selective copper electrodeposition since nucleation and growth is limited to hydride-terminated areas of silicon surfaces. Similar nucleation-inhibition strategies may be used for other deposition methods such as ALD. In another example, covalently grafted nanostructures of 5-hexynoic acid afford in situ chemical activation for selective immobilization of proteins on semiconductor surfaces. Directed placement of organics, proteins, or other biomolecules on silicon surfaces at the nanometer scale may be used to fabricate hybrid silicon-organic-biological devices. In other sensor or biological applications reactive surfaces may be used to anchor polymeric films or immobilize specific biomolecules. In addition to providing a high throughput and facile functionalization process, this method offers opportunities for controlling molecular tethering on silicon surfaces with nanometer scale precision. Clearly, there are many functional groups and potential applications for this versatile electrochemical patterning technique including similar methods for other semiconductor or metal surfaces. The established anodic and cathodic grafting mechanisms may be used to analyze the chemical/mechanical/electrical effects of various electrolyte additives for silicon insertion anodes in secondary lithium batteries.
4. SILICON INSERTION ANODES FOR SECONDARY LITHIUM BATTERIES

4.1 Secondary Lithium Batteries

The fact that hybrid automobile sales increased by a massive seven fold in the first four years, insinuates the future of transportation is strictly poised towards electric vehicles (EV) or hybrid energy vehicles (HEV) systems. (Huggins 2009) Drain of fossil fuels and toxic green house emissions by internal combustion (IC) engines drive the zeal to create better electrochemical systems or batteries for hybrid vehicular propulsion applications. The primary requirement for such an electrochemical system or battery is to provide sufficient range of energy and power comparable to fossil fuels, with excellent rechargeability and long cycle life. It is interesting that while fossil fuels deliver only ~60% maximum energy conversion efficiency, electrical systems or secondary batteries can convert most of the available energy (~99%). The electrochemical systems typically constitute fuel cells, super capacitors and secondary rechargeable batteries. Fuel cells can provide an acceptable range for EV with specific energy highly comparable to fossil fuels, whereas super capacitors present great acceleration with comparable specific power values; however, secondary battery systems provide both specific energy and power in a single entity along with excellent cycle life and rechargeability for EV/HEV applications. While other secondary battery systems provide merely acceptable but relatively lower values for specific energy and power, secondary lithium batteries reply the EV/HEV requirements with 135 Wh/kg specific energy and 320 Wh/liter energy density, well comparable to fossil fuels. (Huggins 2009) Lithium also possesses other beneficial properties such as lightweight (0.53 g/cc) and extremely electropositive nature (-3.04 V
Lithium ion batteries typically constitute metallic lithium electrodes in a suitable electrolyte with a lithium salt as supporting electrolyte. Apart from having the greatest known specific energy capacity, pure lithium electrodes are extremely reactive to moisture and present highly exothermic reactions. Use of organic electrolytes may rectify this limitation and provide acceptable safety levels by inhibiting exothermic surface reactions, but lithium electrodes also suffer from dendrite formation on the surfaces that further leads to an irreversible capacity loss due to short-circuit of the cell. Due to aforementioned limitations, lithium electrodes are typically replaced with relatively cheaper and much safer carbonaceous anodes and lithium metal oxide cathodes. The resulting secondary lithium battery system is more commonly known as the “lithium rocking chair” battery as the lithium ions rock back and forth from anode to cathode and cathode to anode during cycling. In a typical lithium rocking chair, lithium ions may be reduced and intercalated into the carbonaceous anode (typically graphite) during the charging process and are oxidized and disintercalated from the anode during the discharging process. The electrode reactions during charging with a graphite (C) anode and a lithium cobalt oxide (LiCoO₂) cathode are given in reactions 4.1 and 4.2.

(Megahed and Scrosati 1994)

\[
\text{Anode: } x\text{Li}^+ + 6\text{C} + xe^- \leftrightarrow \text{Li}_x\text{C}_6 \quad (4.1)
\]

\[
\text{Cathode: } \text{LiCoO}_2 \leftrightarrow xe^- + \text{Li}_{(1-x)}\text{CoO}_2 \quad (4.2)
\]

As shown in reactions 4.1 and 4.2 each lithium ion requires six carbon atoms during the intercalation/deintercalation process. Commercial graphite anodes offer
specific capacity of ~370 mAh/g in combination with lithium cobalt oxide cathode having a specific capacity of ~200 mAh/g. (Huggins 2009) Although overall cell capacity depends on both anode and cathode specific capacities, current research is strongly focused on developing novel high capacity insertion anodes.

4.2 Silicon Insertion Anodes

Silicon anodes are relatively safe to metallic lithium and offer the best-known theoretical specific capacity of ~4200 mAh/g after lithium via Li4.4Si phase alloy formation. (Huggins 2009) The theoretical specific capacity of silicon is more than ten fold higher than that of graphite (~370 mAh/g), with each lithium ion stored using ~0.22 silicon atoms compared to 6 carbon atoms with graphite anodes. The complete charging reaction with silicon anode is given in reaction 4.3.

Anode: 22Li⁺ + 5Si + 22e⁻ ⇌ Li22Si5  (4.3)

Despite the high capacity, silicon anodes are commercially limited by >300% reversible volume expansion upon complete charging relative to 5% reversible expansion with graphite anodes. Bulk silicon anodes may not tolerate the reversible volume changes and undergo pulverization and subsequent anode cracking, leading to ~90% irreversible capacity loss observed within the first 5 charge/discharge cycles. (Li, Huang et al. 2000) This irreversible capacity loss is often referred to, by the term ‘capacity fade’ and is one of the major barriers preventing silicon anodes for commercial lithium battery applications. Graetz (Graetz, Ahn et al. 2003) reported cracking may propagate via dislocation emission from crack tip; however, the crack should exceed a critical size to propagate, calculated as shown in the equation 4.4. (Graetz, Ahn et al. 2003)
The term $K_{lc}$ stands for fracture toughness and $\sigma$ stands for yield strength, suggesting a critical size of $a_c = 300 \text{ nm}$ for polycrystalline silicon. This calculation propelled a theory that nanostructured silicon anodes with at least one dimension $< 300 \text{ nm}$ may retain their shape and structure during reversible volume changes in cycling; however, experiments with nanocrystalline silicon particles of $< 20 \text{ nm}$ diameter and $100 \text{ nm}$ thick, amorphous silicon thin films as anodes have shown persistent fade behavior. The nanoparticles retained only 50% (of 1100 mAh/g) and thin films retained only 60% (of 3500 mAh/g) of their initial values after 50 cycles. (Graetz, Ahn et al. 2003) Corresponding transmission electron microscopy (TEM) results by Graetz (Graetz, Ahn et al. 2003) confirmed no cracks have been observed on the nanostructured surfaces, suggesting more underlying factors that contribute to the capacity fade apart from cracking due to reversible volume expansion of silicon. In another work, thin film silicon anodes of nanoscale thickness (40 nm) deposited via CVD process have shown high discharge capacities of 3000 mAh/g over 25 cycles. (Li, Huang et al. 1999) While an improved performance with nanoparticles may be achieved by using 10-40% binders and conductive carbon black additives, the initial capacity still does not match that of nanoscale thin films. (Takamura, Ohara et al. 2002) Park et al. (Park, Kim et al. 2009) used a different technique to manufacture silicon powder anodes encapsulated in a TiO$_2$ buffer layer for resisting volume expansion, but the technique has shown limited success as capacity fade still persisted with cycling. The inhibited initial capacity with nanoparticles may be due to the high surface energy of the particles resulting in agglomeration and subsequent capacity loss due to formation of impenetrable blocks. (Park, Kim et al. 2009)
Recent research pathways using silicon nanowires (SiNWs) instead of particles or thin films indicate initial storage capacities up to 90% theoretical value and excellent rechargeability. Chan et al. (Chan, Peng et al. 2008) demonstrated one-dimensional silicon nanowires grown on and directly in contact with conductive gold surfaces as high capacity anodes (~4277 mAh/g initial capacity) for lithium batteries owing to facile strain relaxation, higher porosity and higher surface area per volume ratio relative to other silicon anodes. Lithium insertion was observed to destroy the silicon crystal structure, gradually leading to a metastable amorphous Li-Si alloy. (Li, Huang et al. 2000) Swelling across a single dimension, the length of the nanowires may reduce the surficial damage caused by reversible volume expansion while the direct one dimensional electron pathway of nanowires allows sufficient electron transport; (Chan, Peng et al. 2008) however, the technique is extremely expensive for large scale commercialization, further limited by the quantity of nanowires that can have direct contact with the substrate. On the contrary, Peng et al. (Peng, Jie et al. 2008) demonstrated silicon nanowires grown on silicon wafers through a much cheaper electroless etching technique. The electrolessly etched nanowire anodes withstand the reversible volume expansion and remain intact without pulverization; however, the underlying silicon substrate simultaneously undergoes cracking and pulverization to lose electrical contact with nanowires on surface. Xu et al. (Xu and Flake 2010) used electrolessly-etched nanowires in a composite anode with graphite including a poly (vinylidene fluoride) binder and a conductive carbon black matrix. A target concentration of 15% nanowires was used along with 85% graphite to maximize the overall cell capacity to silicon content ratio based on existing LiCoO$_2$ cathode capacity of 200 mAh/g. (Xu and Flake 2010) Such a composite anode with 15%
nanowires has a theoretical capacity of ~945 mAh/g constituting the active materials. The key advantages of the anode are the stability of silicon due to one dimensional nanowires structure and graphite alleviating the volume expansion of silicon and reducing the overall volume expansion of the anode from 400% (with pure silicon) to ~150% (based on 15% silicon in graphite). But the capacity fade problem still persists indicating there are many underlying factors causing the fade, beside the well-known reversible volume expansion. One of the key factors causing the fade may be associated with the formation of a protective solid-electrolyte interphase (SEI) layer upon the anode surfaces via organic electrolyte dissociation.

4.3 Solid Electrolyte Interphase (SEI)

The most common organic electrolyte used for a lithium ion battery constitutes a 1:1 mixture of dimethyl carbonate (DMC): ethylene carbonate (EC) with a 1 M lithium hexafluorophosphate salt as a supporting electrolyte. In the presence of highly electropositive lithium ions, the organic carbonates dissociate to form a protective layer of organic and inorganic products on the electrode surface. In addition to an unstable electrolyte, surface impurities also may electrochemically react with the electrolyte and become a part of the protective layer. This protective layer of ~40-50 nm thickness is known as the solid electrolyte interphase (SEI) layer and is expected to block exothermic reactions of lithium with anode, offer chemical and electronic passivation to the anode surface, transport lithium ions from electrolyte to the anode surface and maintain mechanical integrity with structural changes in case of insertion electrodes such as silicon. (Huggins 2009) Understanding the chemical/mechanical/electrical aspects of the SEI is hard due to the typical amorphous nature of the products and variation of SEI
composition as a function of distance from the anode surface towards the SEI-electrolyte interface and further with a change of anode or even anode surface chemistry. For example, in case of carbonaceous anodes such as graphite, a major portion of the SEI constitutes lithium carbonates with a trace evidence of lithium alkyl carbonates. In the presence of trace moisture, lithium fluoride formation is observed, whereas the presence of lithium oxide is highly speculated in the initial phases of SEI formation in the vicinity of the anode surfaces.(Huggins 2009) For silicon anodes, SEI plays a crucial role in controlling important factors that in turn control the anode capacity retention. Mechanical integrity and non-conductive/crystalline salt formation in the vicinity of the anode are the chief concerns regarding silicon’s SEI. The SEI should be mechanically strong to address the reversible volume changes of silicon anode. Although SEI formation protects the silicon surface from exothermic lithium reactions, non-conductive/crystalline salt formation may hinder lithium transport through the SEI layer and results in capacity fade with cycling. In this study, chemical, mechanical and electrical aspects of SEI on functionalized SiNWs are investigated in order to identify and inhibit the factors causing the capacity fade with silicon anodes in lithium batteries.

Silicon SEI chemistry is vague from literature as various researchers reported contradictory SEI compositions with silicon. The main reason for the confusion may be due to difference in silicon surface chemistry affecting the SEI composition. Detailed spectral analysis of silicon-SEI products as function of silicon surface chemistry may help to establish and further modify the SEI chemistry as required. An interesting work by Ryu et al.(Ryu, Lee et al. 2008) speculated the following series of SEI reactions on a silicon thin film anode.
POF₃ + 2Li⁺ + 2e⁻ → LiF (s) + LiPOF₂  \hspace{1cm} (4.5)

PF₅ + 2Li⁺ + 2e⁻ → 2 LiF (s) + PF₃  \hspace{1cm} (4.6)

PF₃ + 2Li⁺ + e⁻ → LiPF₂ + LiF (s)  \hspace{1cm} (4.7)

ROCO₂Li (s) + HF → LiF (s) + ROCO₂H  \hspace{1cm} (4.8)

(\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{H}_2\text{O} → \text{Li}_2\text{CO}_3 + \text{CO}_2 + (\text{CH}_2\text{OH})_2  \hspace{1cm} (4.9)

The inorganic fluorophosphates in reactions 4.5-4.7 were identified to be crystalline in nature and may attack the lithiated silicon alloy. Song and Baek (Song and Baek 2009) confirmed the presence of inorganic fluorophosphates products of reactions 4.5-4.8 (LiPOF₂, PF₃, LiPF₂) using ex-situ FTIR analysis. Song and Baek (Song and Baek 2009) further reported formation of PF₅ and PF₃O salts in the presence of trace amounts of moisture in the cell. The silicon surfaces may also undergo chemical effects such as oxidation and fluoride ion attack resulting in irreversible lithium oxide formation near the anode surface and loss of anode material as shown in reactions 4.10-4.12

\[
\text{Si} + 4\text{HF} + 2\text{F}^- + 2\text{h}^+ \rightarrow \text{SiF}_6^{2-} + 2\text{H}^+ + \text{H}_2 \hspace{1cm} (4.10)
\]

\[
\text{SiO}_x + 2x\text{Li}^+ + 2xe^- \rightarrow x\text{Li}_2\text{O} + \text{Si} \hspace{1cm} (4.11)
\]

\[
\text{SiO}^- + 2\text{Li} \rightarrow \text{Li}_2\text{O} + \text{Si} \hspace{1cm} (4.12)
\]

Inhibition of non-conductive inorganic fluorophosphates in the SEI layer along with the silicon surface reactions may inhibit the capacity fade due to silicon SEI chemistry. In this study, combination of conventional surface analysis techniques such as FTIR and XPS are used to establish and monitor the silicon SEI chemistry. Xu (Xu and Flake 2010) reported that nanoscale silicon anodes also suffer mechanical structural damage during reversible volume changes even without cracking. This inherent
mechanical problem is with the SEI unable to maintain contact with the anode under constant volume changes. SEI usually consists of a compact SEI layer near the anode surface and a more diffuse SEI layer towards the electrolyte. A part of the capacity fade may be due to higher contact resistance of the diffuse SEI layer, which may in turn effect the electrical aspects of the anode such as ionic and electronic conductivity. For the first time, AFM force spectroscopy may be applied to measure and compare the stiffness coefficients of anode SEI layers as a measure of mechanical integrity of the anode. Many research articles presented electrical aspects of anode SEI via impedance and mechanical aspects via SEM or AFM experiments; however, a combination of chemical, mechanical and electrical aspects of the SEI established simultaneously may help improve the cycling performance of the anode.

4.4 Functionalized Silicon Anodes

The ability to tailor silicon surface chemistry may allow hybrid inorganic-organic interface engineering and provide an opportunity to improve silicon-SEI interfaces in lithium batteries. Silicon anodes may be functionalized in situ or ex situ in order to study the effects of silicon surface chemistry upon lithiation and improve the SEI aspects for better cycling performance of the anode. Various functionalization strategies have been employed to reduce the capacity fade with nanoscale silicon anodes. Protective carbon coating via pyrolyzed organic monolayers, in situ electrolyte additives, alternative binders and lithium salts constitute the important strategies that may involve modifying the SEI or silicon-SEI interface. Protective carbon coating on anode surface was the preliminary technique used to improve SEI layer chemistry, lithium ion conductivity and inhibit silicon surface reactions. Dimov et al. (Dimov, Kugino et al. 2003) reported carbon
(graphite) coated silicon nanoparticles with a reversible storage capacity of 1500 mAh/g. A similar strategy was used by Kwon et al. (Kwon, Park et al. 2007) by application of butyl capping on silicon nanocrystals via thermal grafting, which is further pyrolyzed at 700 °C to obtain a carbon coating. The technique yielded silicon anode storage capacities of 3000 mAh/g with 84% capacity retention after 30 cycles. Kim et al. (Kim and Cho 2008) reported carbon core-shell nanowires with mesoporous silicon, obtaining 3000 mAh/g storage capacity with 80% initial value retained after 80 cycles. Lee et al. (Lee, Kung et al. 2009) reported pyrolyzed carbon coating obtained via heating a 2-allyl phenol polymer gel electrolyte yielding reversible storage capacity of 2400 mAh/g. The carbon coating technique appears to be effective in reducing the capacity fade but is still limited by the loss of adhesion with SEI layer and subsequent exposure of silicon surface during volume changes over successive charge/discharge cycling; however, it is that the SEI formed on such anodes may be similar to that formed on graphite anodes instead of pure silicon anodes.

Another important anode functionalization technique is to employ in situ electrolyte additives that functionalize the anode surface and SEI continuously during cycling. Trimethoxysilane additives were reported to reduce the capacity fade by suppressing inorganic fluorophosphates in SEI that may otherwise damage the lithiated silicon alloy and other silicon surface reactions such as oxidation. Ryu et al. (Ryu, Lee et al. 2008) reported in situ trimethoxysilane functionalization would replace crystalline inorganic fluorophosphates with amorphous organic fluorophosphates and improve the capacity retention of silicon thin film anodes. Song and Baek (Song and Baek 2009) applied the same trimethoxysilane additive with nanocrystalline silicon
electrodes obtaining 3000 mAh/g initial capacity with 84% of 2nd cycle value retained after 200 cycles. Besides better SEI chemistry, alkoxy silanes are self-assembling in nature and immediately condense upon exposed silicon surface during the volume expansion to provide a complete surface protection against irreversible lithium oxidation. Other electrolyte additives such as vinylene carbonate,(Chen, Wang et al. 2007) maleic anhydride,(Ufheil, Baertsch et al. 2005) fluoroethylene carbonate(Choi, Yew et al. 2006) and maleimide(Wang, Cheng et al. 2009) based cyclic aromatics were also reported to improve anode capacity retention. In one of the recent studies, Ryu et al. proposed trifluoromethyl maleic anhydride instead of maleic anhydride additive might offer relatively easier reduction and greater lithium insertion into silicon electrode. These in situ functionalizations are mostly based on electrochemically reducing the electrolyte additive on the anode surface resulting in a synthetic SEI before ethylene carbonate dissociation results in a natural SEI on the anode. Other notable strategies target minor factors such as alternative binders(Buqa, Holzapfel et al. 2006) (e.g. methyl cellulose) and alternative lithium salts (e.g. LiBOB)(Choi, Yew et al. 2007), suggesting slightly improved capacity retention; however, the main focus of this work is to improve the capacity retention of silicon based composite anodes by engineering a stable silicon-SEI interface. One of the main goals of this study is to establish in situ and ex situ functionalization effects on silicon lithiation. Silicon functionalization may also be used to establish and modify chemical, mechanical and electrical aspects of the silicon SEI in order to improve the cycling performance of the anode.
5. FUNCTIONALIZED SILICON ANODES FOR LITHIUM BATTERIES*

5.1 Introduction

The inability to tap and retain the full theoretical capacity of silicon (~4200 mAh/g) calls for novel tools that could help investigate the underlying factors contributing to the fade, such as the SEI layer. In this study, various SEI aspects were demonstrated as a function of silicon anode surface chemistry. As the SEI aspects were realized to be a function of anode surface, silicon presents an incredible opportunity to analyze the SEI as a function of controlled surface chemistry. Typically, most researchers do not mention the surface chemistry of silicon anode employed, which results in different anodes showing different SEI chemistries with silicon. Chan et al.(Chan, Ruffo et al. 2009) demonstrated native oxide terminated SiNW anodes show lower capacity fade relative to hydride terminated SiNW anodes. In this study, various organic functionalized SiNW surfaces are investigated to improve anode capacity retention and silicon-SEI interface quality. SiNW based anode surfaces are functionalized via ex situ electrografted organic monolayers or self-assembled organosilane monolayers and in situ electrolyte additives. Ex situ functionalization may be used to manipulate the silicon-SEI interface. In situ organosilane electrolyte additives are used to stabilize the SEI layer to improve the reversible storage capacity of SiNW based composite anodes. The functionalized anodes may be characterized via cyclic voltammetry and ex-situ FTIR/XPS analysis to identify and compare the corresponding SEI chemistries. AFM force spectroscopy is used for the first time in order to establish the contact stiffness values and compare the mechanical integrity of functionalized SEI layers. The

corresponding electrical parameters may be investigated by electrochemical impedance spectroscopy. The established chemical, mechanical and electrical parameters of the silicon SEI may help improve the capacity retention of SiNW based composite anodes.

5.2 Experimental

5.2.1 Anode Preparation

Two types of anodes were used in this study; electrolessly etched SiNW arrays on bulk silicon substrates and SiNW based composite anodes. For SiNW arrays, bare silicon wafers, cleaned in HF, were immersed in a solution of 5 M hydrofluoric acid and 0.02 M silver nitrate and heated at 50 °C for 40 min. The resulting wafers were cleaned in a series of steps with DI water, 1:1 nitric acid: DI water and pure DI water again to yield dense nanowire arrays. SiNW arrays thus obtained, with/without functionalization were as such applied as anodes for SEI analysis. In situ and ex situ functionalizations were applied to nanowire arrays before the nanowires were separated from parent wafer via sonication in a transfer solvent or by manual scratching. For composite anodes, graphite was mixed with a binder material such as poly (vinylidene fluoride) (PVDF) and n-methyl pyrrolidone (NMP) solvent and carbon black filler material to make a slurry. The nanowires with/without functionalization, are dried and weighed before adding the required weight percentage (15% SiNWs relative to graphite) to the slurry. As NMP evaporates, the slurry becomes a homogenous paste, which was further deposited onto a nickel or copper metal foil acting as a current collector. Approximately 100-500 µm thick films were created on nickel or copper electrodes, corresponding to a theoretical specific charge capacity of 945 mAh/g, based on active materials alone calculated as per the equation 5.1.
\[ C_{total} = (W_g*372) + (W_s*4200) \]  

(5.1)

where \( W_g \) and \( W_s \) represent the weight percentages of graphite and silicon nanowires respectively. The composite anodes deposited on nickel or copper current collectors are further baked at 120 °C for 12 hours before using the anodes for battery experiments to obtain a final composition of 51% graphite, 9% SiNWs, 20% PVDF and 20% carbon black. For functionalized composite anodes, the SiNWs are functionalized as arrays prior to separation from parent wafer.

5.2.2 Anode Functionalization

Hydride, methyl, methoxy and trimethoxymethyl silane functionalizations were applied to SiNW arrays in this study. Hydride surfaces were obtained by dipping the SiNW arrays in 10 % hydrofluoric acid for 1 minute. Methylated (100) surfaces with 1:1 methyl: hydride molecules per surface silicon were prepared via electrografting SiNW arrays at a constant potential of 0.1 V versus Ag/AgCl for 120 s. Ex situ trimethoxymethyl silane monolayers were obtained via treating the nanowire arrays with trimethoxymethyl silane precursor for 24 h. The ex situ functionalized SiNW arrays may as such be used for battery experiments. For application in composite anodes, the functionalized nanowires are manually scratched from the surface, as sonication may disturb the monolayer packing and is not recommended. For in situ trimethoxymethyl silane electrolyte additive functionalization, 5% trimethoxymethyl silane is added to 1:1 DMC: EC electrolyte prior to the experiments with either nanowire array or composite anodes.
5.2.3 Characterization

A typical three-electrode setup with SiNW array anodes and lithium metal counter and reference electrodes, is used to measure the charge/discharge behavior of SiNW array or composite anodes. SiNW arrays or composite anodes (deposited onto a metallic current collector) were connected as the working electrode against lithium foil counter and reference electrodes. An organic electrolyte of 1:1 dimethyl carbonate/ethylene carbonate (DMC/EC) with 1 M LiPF$_6$ lithium salt was used as the ionic pathway between the electrodes. The charge/discharge and electrochemical impedance analysis measurements were conducted using the same three-electrode setup with a PARSTAT 2273 potentiostat. The SiNW array anodes were charged from 1.5 V (vs. Li/Li$^+$) to 0.01 V (vs. Li/Li$^+$) and discharged from 0.01 V (vs. Li/Li$^+$) to 1.5 V (vs. Li/Li$^+$) using cyclic voltammetry. The composite anodes were charged at constant current density of -25 $\mu$A/cm$^2$ and discharged at a current density of +25 $\mu$A/cm$^2$ for 100 ks with a lower limit for charging at 0.01 V (Vs. Li/Li$^+$) and upper limit for discharging at 1.5 V (vs. Li/Li$^+$) for each cycle. The first charge/discharge cycle was considered the conditioning cycle to allow formation of uniform SEI layer on the surface. The anodic specific charge capacity was calculated by integrating the area under the charge/discharge chronopotentiometry plots for each cycle after the conditioning cycle. Infrared spectra were acquired using a Nicolet (Thermo Scientific, Madison) Model 380 FTIR with multi-bounce ZnSe waveguide while 512 scans (2 cm$^{-1}$ resolution) were taken using a Deuterated Triglycine Sulfate (DTGS) detector. X-ray photoelectron spectroscopy (XPS) data were collected on Axis 165 photoelectron spectrometer (Kratos Analytical) with the collection chamber maintained at 1.5 x 10$^{-9}$ Torr. An incident beam of soft X-rays (160 keV) from an Al K$\alpha$
source was injected at an incident angle of 90°. AFM force spectroscopy was conducted using an Agilent 5500 AFM/SPM system equipped with Picoscan v5.3.3 software. V-shaped non-conductive silicon nitride cantilevers (MSCT-AUNM, resonance frequency 120 kHz, spring constant 0.5 N/m) were obtained from Veeco (Portland, OR) and an ambient environment was used for ex situ force spectroscopy. The electrochemical impedance spectroscopy measurements were obtained at no DC bias and an AC amplitude of 10 μA within the frequency range of 100 μHz – 1 MHz.

5.3 Results and Discussion

5.3.1 SEI Analysis on SiNW Arrays - Cyclic Voltammetry

Cyclic voltammetry was used to investigate silicon functionalization effects on corresponding SEI layer formation with SiNW array anodes in lithium half-cells. Figure 5.1 shows the cyclic voltammogram plots for ex situ hydride, methyl, trimethoxymethyl silane and in situ trimethoxymethyl silane functionalized SiNW array anodes. None of the array anodes showed any discharge behavior; however, at <0.2 V (vs. Li/Li+) variable current densities were observed with different terminal chemistries. Electrografted methyl and ex situ trimethoxymethyl terminations show inhibited lithiation and organic electrolyte reduction relative to bare nanowires (hydride). This may be attributed to greater energy requirement for lithiation of passivated anodes (Vegunta, Ngunjiri et al. 2009). In contrast, in situ 5% trimethoxymethyl silane additive in the electrolyte significantly enhanced the lithium insertion current density relative to hydride terminated SiNW arrays within the same potential window. This could be attributed to more lithiation of in situ siloxane functionalized anodes relative to hydride-terminated
anodes resulting in a greater exposure of pristine silicon available for electrolyte reduction.

From cyclic voltammetry results in Figure 5.1, it is important to note that the lithiation onset potentials vary with each applied functionalization. While ex situ trimethoxymethyl silane does not show any lithiation onset within the potential window, ex situ methyl surface shows lithiation onset at ~0.1 V (vs. Li/Li$^+$); however, the current density of the methyl lithiation peak is much lower than hydride or in situ trimethoxymethyl functionalizations.

![Cyclic voltammetry of hydride terminated, electrografted methyl terminated silicon nanowire arrays (SiNWs), SiNWs with 5% trimethoxymethyl silane additive in the electrolyte and SiNWs pre-functionalized with trimethoxymethyl silane. (Xu, Vegunta et al. 2011)](image)

Hydride surfaces also show a considerable lithiation peak at ~0.1 V (vs. Li/Li$^+$); however, hydride surfaces show a two-fold greater current density relative to the methyl
surfaces. The identical lithiation onsets with difference in current density may be due to
similar lithium adsorption potentials but reduced lithium transport across the silicon-
methyl-SEI interface relative to hydride. The inhibited lithium transport across the
methylated surfaces may be due to high impedance of methyl monolayers relative to
hydride as indicated in chapter 3.3.7. Compared to hydride and methyl surfaces, in situ
trimethoxymethyl silane functionalized anodes show more anodic lithiation onset (~0.35
V vs. Li/Li\textsuperscript{+}) along with greater current density.

5.3.2 SEI Analysis on SiNW Arrays – Ex situ FTIR Analysis

Ex situ FTIR analysis spectra were obtained after subtraction from corresponding
electrolyte spectra, as shown in Figure 5.2. Bare SiNWs show a strong peak at \( \sim 834 \text{ cm}^{-1} \)
which can be assigned to inorganic PF\textsubscript{x} compounds from electrolyte reduction (Song and
Baek 2009). Visible peak at \( 1607 \text{ cm}^{-1} \) suggests the carbonyl group RCO\textsubscript{2}M\textsuperscript{m+} where M
represents Li/Si alloy and R represents alkyl group. Small peaks at 1275 and 1023 cm\textsuperscript{-1}
are attributed to stretching mode of P=O and asymmetric stretching mode of P-O-C from
\(-O=PF-OR\) group. The peak at \( 1108 \text{ cm}^{-1} \) is attributed to silicon oxide species. The
results confirm that the electrolyte was reductively decomposed resulting in the formation
of a typical silicon-SEI interface. FTIR spectra for electrografted methyl show no peaks
for electrolyte reduction products as expected. Only a major characteristic peak at 835
\text{ cm}^{-1} \) is observed, which is attributed to the PF\textsubscript{x} compounds. Clearly the methyl monolayer
could not diminish PF\textsubscript{x} composition in the SEI layer.

For in situ trimethoxymethyl silane, subtracted FTIR spectra show a relatively
high intensity peak at \( 1611 \text{ cm}^{-1} \) confirming the presence of carbonyl group RCO\textsubscript{2}M\textsuperscript{m+}
suggesting greater electrolyte reduction on the anode relative to bare SiNWs. Intensity
was much higher at 1156 cm\(^{-1}\) associated with asymmetric Si-O-Si stretching, and at 1385 cm\(^{-1}\) indicating the Si-C stretching suggesting the formation of a “silicon-rich SEI layer”, with a silane network in the SEI. Also, the silicon-rich SEI layer indicates an enhanced peak at 823 cm\(^{-1}\), which could be assigned to the presence of silanol groups. The inorganic fluorophosphates (835 cm\(^{-1}\)) were diminished with 5% silane additive in the electrolyte. This is mainly attributed to the enhanced organic electrolyte reduction and simultaneous silane condensation in the SEI during initial charging cycle. 5% silane additives were further applied in composite anodes to verify the proposed strategy for inhibiting capacity fade.

Figure 5.2 Ex-situ FTIR analysis of SEI layer formed after the initial charging cycle upon A. SiNWs, B. SiNWs with 5% trimethoxymethyl silane additive in the electrolyte and C. SiNWs electrografted with methyl monolayers.
5.3.3 SEI Analysis with SiNW Arrays - Ex-situ XPS Analysis

Ex situ X-ray photoelectron spectroscopy was used to analyze the SEI chemistry and support the FTIR data shown in Figure 5.2. Figure 5.3 shows the C 1s, F 1s and O 1s XPS spectra for bare (hydride terminated), electrografted methyl, trimethoxymethyl silane functionalized SiNW surfaces. The C 1s spectra are obtained over a binding energy range of 280-294 eV to investigate the carbon bound species as shown in Figure 5.3. Hydride terminated surfaces show C-O and C=O peaks (~286 eV) associated with carbonates in the SEI, along with a relatively high intensity peak at ~291 eV associated with carbon species bound to electronegative fluorine group from the electrolyte. The organofluorine compounds are not reported on graphite, while observed by Chan et al. (Chan, Ruffo et al. 2009) with SiNW anodes directly grown on metal current collectors. Similar results were obtained in our study, but only on hydride and M silane surfaces but not on methylated surfaces. This suggests the C-F compounds are surface-selective and may play a crucial role in controlling silicon SEI chemistry. The fact that C-F compounds were observed only with hydride and in situ siloxane monolayers suggest a positive correlation with the corresponding cyclic voltammetry peaks obtained at ~0.5 V (vs. Li/Li+) as shown in Figure 5.1.

Figure 5.3 also shows the O 1s and F 1s spectra for the three functionalized SiNW array anode surfaces with binding energy ranges of 526-542 eV and 678-696 eV respectively. The O 1s spectra show similar peaks at ~533 eV with trimethoxymethyl silane and hydride surfaces. The peaks are mainly associated with oxygen bonded to carbon in carbonates. The O 1s spectrum of methylated surface also shows a broad peak at 534.2 eV with a 1.2 eV positive shift in binding energy relative to hydride surfaces.
This may be associated with a combination of C-O and POF_x species of organic fluorophosphates. The F 1s spectra also show similar behavior with hydride and silane showing identical peaks at 686.6 and 686.4 eV respectively, associated with C-F species. As illustrated in C 1s spectra, C-F compounds are not observed with methylated surfaces suggesting that the peak at 688.2 eV obtained in F 1s spectrum of methyl functional surface may be associated with lithium fluoride.

![X-ray photoelectron spectra](image)

Figure 5.3 X-ray photoelectron spectra of C 1s, F 1s and O 1s regions for the SEI formed upon bare SiNWs (Si-H), SiNWs electrografted with methyl monolayers (Si-CH_3) and SiNWs with in situ 5% trimethoxymethyl silane additive in the electrolyte after the initial charging cycle. (Xu, Vegunta et al. 2011)

A mechanism is proposed to explain the formation of C-F compounds observed in XPS analysis. The selective nature of C-F formation on silicon and not graphite suggests the formation is either due to surface chemistry or silyl radical formation. As the C-F
formation is observed with both hydride and methyl siloxane monolayers, silyl formation would be the more likely cause. Crystalline nanowires undergo amorphization process during initial lithiation stages during which silyl radicals are formed. While amorphization, internal defects in silicon show up on the surface due to volume changes and the exposed surface would be extremely reactive. As ethylene carbonate (EC) dissociates via acidic deprotonation a carbonyl radical is formed that would react with the free fluoride ions from trace HF in the electrolyte. Ryu et al. (Ryu, Lee et al. 2008) previously explained trace amount of HF formation with silicon anodes as given in equation 5.2.

$$\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{PF}_3\text{O} + 2 \text{HF} \quad (5.2)$$

The result is a fluorine substituted EC formation, which explains the C-F peak in XPS results. Methylated surface did not show much of EC dissociation and hence the C-F formation is not observed. A schematic of the mechanism is given in Figure 5.4.

Figure 5.4 Schematic for the mechanism of organofluorine formation in the SiNW-SEI.

The XPS results also show the presence of silicon-rich species in the SEI, speculated due to the presence of Si-O-Si species. Uncycled SiNW Si 2p spectra typically
show two peaks at 99.2 eV and 103.6 eV corresponding to silicon and native silicon oxides as shown in chapter 2.3.4. Figure 5.5 shows the Si 2p spectra of cycled bare SiNWs (Si-H) and in situ silane functionalized SiNWs after 1 cycle. The bare SiNWs show typical silicon spectrum as expected, while silane functionalized SiNWs show a relatively low intensity silicon peak at 99.3 eV and a positively shifted peak at 104.3 eV corresponding to Si-O-Si or Si-O-C bonds in the SEI.

![Si 2p XPS spectra](image)

Figure 5.5 Si 2p XPS spectra of the SEI formed upon bare SiNWs (Si-H) and SiNWs with in situ 5% trimethoxymethyl silane additive in the electrolyte after the initial charging cycle.(Xu, Vegunta et al. 2011)

5.3.4 Charge/Discharge Studies with Composite Anodes

Specific energy capacity plots were obtained for bare (hydride), ex situ methylated, in situ 5% trimethoxymethyl silane and ex situ trimethoxymethyl silane functionalized SiNW (15%) composite anodes, along with conventional graphite anodes. Figure 5.6 shows the specific charge/discharge capacities for the functionalized anodes plotted as function of cycling for the first 10 cycles. The data points were obtained by
integrating the area under corresponding chronopotentiometry curves for each cycle. Pure graphite anodes show a reversible discharge capacity of ~315 mAh/g after 10 cycles, which is enhanced to 512 mAh/g using 15% SiNWs in the composite anode; however, a loss of ~300 mAh/g from the initial capacity (811 mAh/g) was observed equivalent to a 37% fade of initial cycle value. Electrografted methyl monolayer shows reduced charge/discharge capacities compared to bare SiNWs with hydride functionalization due to the insulative nature of the methyl monolayer. Initial charging cycle shows a reduced capacity of ~580 mAh/g due to inhibited silicon lithiation as indicated in cyclic voltammetry results (chapter 5.3.1). Discharge plots with 5% trimethoxymethyl silane additive show a reversible capacity of 722 mAh/g after 10 cycles indicating significantly lower capacity fade of ~11% relative to composite anodes with no silane additive.

Figure 5.6 Charge/Discharge data for specific capacity for composite anodes with 100% graphite, 15% SiNWs, 15% methyl-SiNWs and 15% SiNWs with 5% silane electrolyte additive.
Figure 5.7 shows the discharge capacities of silicon alone after subtracting the corresponding graphite capacity for the first 15 cycles. As explained earlier, insulative methyl and ex situ trimethoxy methyl silane functionalizations show inhibited lithiation/delithiation of nanowires with \(~500\) mAh/g reversible silicon discharge capacity after 15 cycles. Bare SiNW based composite anodes with hydride termination show a reversible silicon capacity of \(\sim1500\) mAh/g whereas in situ trimethoxymethyl functionalization demonstrate an excellent reversible silicon capacity of \(\sim2500\) mAh/g with 67% improved capacity retention relative to hydride termination.

Figure 5.7 Functionalized silicon discharge capacities in composite anodes with 15% SiNWs and 85% graphite. Bare (hydride terminated), electrografted methyl, ex situ trimethoxymethyl silane and in situ 5% trimethoxymethyl silane electrolyte additive functionalizations were used. (Xu, Vegunta et al. 2011)

A silicon-rich SEI layer formed in the case of in situ trimethoxymethyl silane inhibits the formation of inorganic fluorophosphates and results in subsequent passivation
of the exposed silicon surface while allowing lithiation. From specific capacity plots and cyclic voltammetry results, the silicon-SEI formation with functionalized SiNW based anodes may be positively correlated with silicon lithiation and delithiation capacities.

5.3.5 SEI Analysis on SiNW Arrays - AFM Force Spectroscopy

Mechanical aspects of the silicon-SEI layers were investigated using AFM force spectroscopy via nanoindentation technique for the first time. Scanning probe microscopy (SPM) based techniques including AFM imaging of SEI morphology were previously reported on graphite (Alliata, Kotz et al. 2000; Leroy, Blanchard et al. 2005) and tin (Lucas, Pollak et al. 2009) anodes; however, AFM force spectroscopy technique has never been used to analyze the SEI mechanical aspects. Vanlandingham conducted a wide range of AFM force spectroscopy and nanoindentation studies on various polymers to investigate the mechanical aspects such as elastic modulus and lateral friction. (Vanlandingham, McKnight et al. 1997; Vanlandingham, McKnight et al. 1997; VanLandingham, Nguyen et al. 2001; VanLandingham, Villarrubia et al. 2001) In this study, methods to establish adhesion forces between the tip and the anode-SEI or the SEI contact stiffness at a given XY location were demonstrated. In this technique, the SiNW array anode with the SEI layer is gradually brought into contact with a non-conductive silicon nitride tip (Veeco probes, Model MSCT-AUNM) mounted on an Agilent 5500 AFM tool (operated in contact mode) and allowed to stay in contact with the surface for 60 seconds. Using Picoscan software, tip deflection is measured as a function of Z-distance from -1000 to +1000 nm. Initially the tip approaches the surface and then pulled off at a constant tip-speed of 100 nm/s. Figure 5.8 shows the deflection vs. distance
profile for the SEI layer on a SiNW array after cycling with/without in situ silane functionalization.

From Figure 5.8A, the profile in red indicates the approach curve (from 1000 to -1000 nm) with a constant deflection voltage till -550 nm where a rapid drop is observed before a linear increase. The constant deflection corresponds to zero external load while the rapid drop indicates that the tip is attracted to the surface when came into the vicinity of the sample due to Vanderwaal’s forces. The linear region corresponds to a gradual increase in force as the tip is indented into the SEI layer. From Figure 5.8A, the profile in blue represents the pull-off section (from -1000 to 1000 nm) where initially the applied force is alleviated during the linear region and the tip stays attached to the sample due to adhesion energy until a sudden increase in deflection is observed at -250 nm where the tip comes off the surface. The pull off spectrum does not necessarily follow that of approach due to the intermolecular bonding or adhesion forces between the tip and the sample.

Figure 5.8 Deflection Vs Z-distance profile for the SEI layer on a NW array anode; A. without silane and B. with silane additive to the electrolyte.
The spectra hold valuable information regarding the tip/SEI contact stiffness in the linear region of the approach spectrum and adhesion forces between the tip and the SEI in the hysteresis due to rapid leap in deflection voltage in the pull-off spectrum. From Figures 5.8A and 5.8B, greater hysteresis is observed in the pull-off section for SEI without silane compared to that of SEI with silane indicating greater adhesion energy between the silicon nitride tip and SEI without silane. This may be explained by difference in attraction forces of silicon nitride tip with siloxane-rich SEI and hydride-SEI. Also, SEI with siloxane shows almost vertical slope in the approach linear region relative to that of SEI without silane. This indicates SEI with silane has greater contact stiffness relative to that of no silane. In order to quantify the effect, the deflection versus distance data were converted to external load versus depth as per the equation 5.3,

$$F = k \times \alpha \times V$$

(5.3)

where $k$ is the spring constant of the cantilever, $\alpha$ is the deflection sensitivity (nm/V) measured from the slope of the linear region when the tip is pressed against a hard surface (bulk silicon in this case) and $V$ is the difference between deflection voltage at a given distance and that of the constant region (zero load). As the spectra are obtained using the same tip, the values of $k$ and $\alpha$ are same for SEI with/without silane.

Figure 5.9 shows the linear regions in external load versus depth profiles for approach spectra of SEI layers with/without silane functionalization. The slope of the linear region correspond the contact stiffness value of the surface at the given XY location. SEI with silane has a contact stiffness of 0.9568 N/m whereas that without silane has a contact stiffness of 0.429 N/m with the silicon nitride tip. Higher stiffness (~125%) with silane indicates the plasticizing effect of silane on a floppy SEI with weak
intermolecular forces. The results indicate in situ silane provides stability against mechanical disintegration of the SEI layer during cycling and prevents subsequent contact loss with the anode substrate. The contact stiffness calculations could further provide corresponding Young’s modulus estimation for the nanoscale layers such as SEI on SiNW based anodes.

![Figure 5.9](image)

Figure 5.9 External load versus Z-depth profiles for SEI layers with/without silane functionalization.(Xu, Vegunta et al. 2011)

5.3.6 SEI Analysis – Electrochemical Impedance Spectroscopy

Impedance analysis is used to identify the electrical properties of the silicon-rich SEI layer. Impedance plots were obtained for SiNW arrays with/without the surface and electrolyte additive functionalizations. From Figure 5.10A, magnitude at DC frequencies is observed to decrease with cycling corresponding to a conductive SEI formation. Two different phase peaks are observed corresponding to two grain boundaries of the anode, the nanowires and the bulk silicon substrates as shown in Figure 5.10B. The constant reduction of the phase peak at 0.01 Hz frequency with cycling suggests the reduction of
double layer capacitance of the nanowires due to the SEI formation. The SEI formation provides a more resistive route rather than the capacitive route for ionic transport. The other phase peak did not change much indicating the electron tunneling effects of nanowire anodes to the current collecting bulk substrate underneath. This suggests the bulk surface is in tact when the nanowire arrays are used as anodes for lithiation/delithiation cycling. The EIS spectra are as shown below.

Figure 5.10 Bode impedance magnitude and phase plots for Hydride terminated silicon surface before 1\textsuperscript{st}, 2\textsuperscript{nd}, 10\textsuperscript{th} cycles and after charging in the 1\textsuperscript{st} cycle.

Bode impedance plots were obtained for composite anodes with/without silane additive, before the conditioning cycles within a frequency range of 0.1 mHz to 1 MHz. Figure 5.11A shows the magnitudes of impedance while Figure 5.11B shows the corresponding phase behavior. At near DC frequencies, the overall impedance magnitude of bare composite anodes was slightly more than that of silane additive anodes. This indicates the addition of 5\% trimethoxymethyl silane also enhanced the electrolyte conductivity. The impedance magnitude near DC frequencies for the 5\% silane additives after the conditioning cycle (~5000 ohms) was much less than the pre-conditioning magnitude (~50000 ohms), which is consistent with the formation of a conductive SEI.
layer on the composite anode surface. The magnitude behavior did not show any major differences from the post conditioning cycle till the 13\textsuperscript{th} cycle with both the anodes with and without silane additive. The DC impedance of nanowire arrays was measured to be of the order of $\sim 10^5$ ohms. Although DC impedance was slightly reduced during the successive charge/discharge cycles, the value was way higher than the DC impedance of a composite anode after the conditioning cycle. This is mainly due to the formation of a conductive SEI layer on the composite anode surface due to enhanced organic electrolyte reduction on conductive graphite compared with the nanowires. (Xu, Vegunta et al. 2011)

![Figure 5.11 Impedance analysis with A. Bode Z plots and B. Bode phase plots of composite anodes with and without 5% trimethoxymethyl silane additive in the electrolyte.](image)

From Figure 5.11B, two sharp, distinct capacitive peaks were observed for anodes with no silane, corresponding to the double layer capacitances of graphite and SiNWs. The peaks shifted to a lower frequency during the cycling suggesting an increase in the double layer capacitance due to the formation of a more conductive SEI layer on the surface. This shift in double layer capacitance due to dielectric layer was earlier observed with impedance analysis of monolayers in aqueous acidic electrolytes. The results clearly
identify better conductivity of the silicon-rich SEI layer formed in the presence of silane additives lead to better capacity retention of SiNW based composite anodes and future work focuses upon improving conductivity of the SEI layer via functionalization with conductive polymer materials.

5.4 Conclusions

Direct or indirect organic functionalizations were applied to improve the silicon-SEI chemistry with SiNW array anodes and inhibit the capacity fade in SiNW-based composite anodes. Cyclic voltammetry and ex situ FTIR results indicate in situ alkoxy silane additives would enhance silicon lithiation while inhibiting inorganic fluorophosphates in the SEI that may otherwise damage the lithiated silicon alloy. Cyclic voltammetry results further suggested silicon lithiation may be a function of surface chemistry. This speculation is researched in detail in the next chapter, with a variety of in situ and ex situ functionalized silicon anodes. Ex situ XPS results offered further support to FTIR data and shows the presence of organofluorine compounds in the SEI. A suitable mechanism has been proposed for the formation of organofluorines in SiNW-SEI layers. Ex situ XPS results also provided sufficient evidence to the presence of silicon-enriched SEI obtained with in situ alkoxy silanes. Charge/discharge cycling results with in situ alkoxy silanes in the electrolyte inhibit silicon capacity fade and demonstrate improved reversible lithium storage capacity of silicon by 67% after 15 cycles relative to bare (hydride terminated) SiNW based composite anodes. For the first time, AFM force spectroscopy technique was applied to analyze the mechanical contact stiffness of the functionalized SEI layers. In situ silane functionalized SEI layers show ~125% greater contact stiffness than the ex situ hydride SEI layers, most likely due to the mechanical
reinforcement of an otherwise floppy hydride SEI layer via silane cross-linking. Impedance analysis established conductive SEI layer was formed in composite anodes due to electrolyte reduction on graphite, which are electrically linked to silicon anodes by formation of a silane network in the SEI. It appears that the in situ silane functionalization improved the chemical and mechanical parameters of the silicon-based anodes without showing much effect on the electrical aspects. Further, in situ functionalized SiNWs may be electrically contacted to the nickel current collector surface via NiSi alloy formation to improve the electrical characteristics of the silicon-SEI interface.
6. FUNCTIONALIZED SILICON-SEI INTERFACES FOR LITHIUM BATTERIES

6.1 Introduction

Silicon anodes offer an excellent alternative to unsafe metallic lithium, with 10 fold greater theoretical capacity relative to conventional carbonaceous anodes; however, silicon anode commercialization is limited by ~300% volume expansion causing cracks and pulverization of anode, resulting in capacity fade. Nanoscale silicon anodes with atleast one dimension less than 300 nm may prevent fade due to crack propagation, but significant capacity fade (loss of >20 % of initial capacity) persists.(Graetz, Ahn et al. 2003) SiNWs manufactured via direct nucleation on metallic current collectors have shown excellent capacity retention (~90% initial value) due to the ability to withstand silicon volume changes and one-dimensional electron transfer(Chan, Peng et al. 2008); however, the technique is expensive and is limited by low SiNW throughput via nucleation process. Xu et al.(Xu and Flake 2010) reported manufacturing of SiNWs in bulk that can be separated from parent wafer and later used in a composite anode along with graphite. Two-fold greater capacity was reported by adding just 15% by weight SiNWs in composite with graphite; however, capacity fade persisted with composite anodes within the first 10 cycles.

In the previous chapter, significant capacity loss of ~32% after just 10 cycles with SiNW-graphite composite anodes was reduced to <20% after 15 cycles via in situ trimethoxymethyl silane functionalization. Chemical, mechanical and electrical aspects of the SEI layer formed on hydride and in situ trimethoxymethyl silane functionalized SiNW arrays were investigated in detail to understand and inhibit the fade mechanism. In
situ trimethoxymethyl silane functionalization provides better SEI chemistry and cross-linking of Si-O-CH₃ branches with carbonates in the electrolyte, offering better mechanical stiffness and lower contact resistance to an otherwise floppy SEI layer with hydride termination. Further cyclic voltammetry results suggest an interesting observation that the silicon lithiation may be a function of surface chemistry. In this chapter, silicon lithiation is further established as a function of various in situ and ex situ surface functionalizations upon SiNW array anodes. Ex situ native oxide, hydride, methyl and methoxy functionalized surfaces and in situ trimethoxymethyl silane (M silane), triethoxyfluoro silane (F silane), vinylene carbonate (VC) and trifluoromethyl maleic anhydride (TFMMA) electrolyte additive functionalizations were used with SiNW array anodes to investigate silicon lithiation. The ex situ terminal functionalizations used in this study were chosen to constitute both electron donating and electron withdrawing groups such as methyl and methoxy respectively. Chan et al.(Chan, Ruffo et al. 2009) previously reported native oxide-terminated nanowires show better capacity retention relative to HF etched SiNWs due to high reactivity of hydride surfaces. The in situ functionalizations were chosen based on our previous studies (chapter 5) and literature review (chapter 4).

In the previous chapter, in situ functionalized SiNW-graphite composite anodes were reported with acceptable capacity retention up to atleast 15 cycles. In this chapter, individual nanowires were electrically contacted with nickel current collector in bulk to achieve enhanced electrical aspects of the silicon-SEI interface and investigate the cycling ability of individual SiNWs. This may be achieved via NiSi electrical contact by heating the SiNWs deposited on nickel surface (NiSiNWs) in a reducing atmosphere as reported by Xu et al.(Xu, Palshin et al. 2009) Suitable combination of in situ and ex situ
functionalizations was applied to NiSiNW anodes for better lithiation and to investigate interface cycling characteristics, SEI chemistry and electrical parameters of the SEI. The functionalized anodes may be characterized via cyclic voltammetry, SEM, ex situ FTIR and impedance spectroscopy techniques.

6.2 Experimental

Silicon wafers (p-type, 1-5 Ω⋅cm) were obtained from Montco silicon and nickel metal (99.99%) was obtained from ESP Metals Inc. All the chemicals used in this study were obtained from Sigma Aldrich unless specified otherwise. Triethoxyfluoro silane (F silane) and trifluoromethyl maleic anhydride (TFMMA) were obtained from Matrix Scientific. SiNW arrays were manufactured electrolessly as reported in the previous chapter. For NiSiNW anodes, the nanowires were first separated from the parent wafer and deposited on nickel surface via a transfer solvent such as acetone. It is crucial that the nanowires in transfer solvent be sonicated for atleast one minute to minimize nanowire agglomeration during the deposition. Nickel surfaces with deposited SiNWs were then heated at 450 °C for 30 min., before cooling down to room temperature in a reducing atmosphere (40% H₂ in N₂). SiNW arrays and NiSiNW anodes were then functionalized in situ or ex situ as required.

SiNW arrays and NiSiNWs anodes were as such heated on a hot plate at 200 °C for 6 hours exposed to ambient air for native oxide termination. The anodes were treated with 10% HF for 1 minute to obtain hydride termination. Methyl termination was obtained by electrografting anode surfaces in methyl Grignard solution at 0.1 V (vs. Ag/AgCl) potential for 120 s. The methyl Grignard surfaces were passivated against native oxide formation for 55 days as reported in chapter 2. The electrografted methyl
monolayer on (100) surface yields a 1:1 methyl: hydride termination per each surface silicon. (Vegunta, Ngunjiri et al. 2009) Methoxy termination may be obtained following heating the anode substrates in methanol solutions at 65 °C for 3 hours. The procedure is reported earlier by Michalak et al. (Michalak, Amy et al. 2010), who further reported the maximum surface coverage with methoxy termination is limited to 33% with rest of the surface oxidized. For in situ functionalization, 5% (by volume) corresponding precursor is added to the lithium battery electrolyte. The functionalized anodes were characterized via cyclic voltammetry, SEM, FTIR and impedance analysis. Electrochemical measurements including cyclic voltammetry and EIS were performed via a PAR 2273 potentiostat. Ex situ FTIR spectra were obtained using a Nicolet 380 model multi-bounce ZnSe waveguide as 512 scans were taken with 2 cm⁻¹ resolution and DTGS detector. EIS measurements were performed after equilibration at each specified potential for 2 hours within a frequency range of 1 mHz to 1 MHz.

6.3 Results and Discussion

6.3.1 Lithiation versus Ex situ Functionalization

Silicon lithiation is demonstrated as a function of silicon surface chemistry via cyclic voltammetry and double differential charge density versus potential plots. Cyclic voltammograms for native oxide, hydride, electrografted methyl and thermally grafted methoxy terminated SiNW array anodes, obtained at 0.4133 mV/s (~C) scan rate are as shown in Figure 6.1. The voltammograms ranging from 1.5 to -0.5 V (vs. Li/Li⁺) show great reduction current densities at higher potentials (1.5 to 0.5 V vs. Li/Li⁺) associated with corresponding SEI layer formation. A faster scan rate is employed mainly in order to focus the investigation more on the silicon-SEI interface rather than the SEI itself. From
Figure 6.1, it appears that the lithiation onset potentials vary over ~400 mV range of potentials from ~0.1 V to -0.3 V vs. Li/Li\(^+\) for the functionalized anodes. Native oxide surface shows the most anodic onset potential at ~0.1 V vs. Li/Li\(^+\) while the electrografted methyl shows the most cathodic onset potential at ~300 mV. To clearly obtain the lithiation onset potentials, double differential charge versus voltage plots were obtained by differentiating the cyclic voltammogram data shown in Figure 6.1.

![Graph showing potential vs. current density for native oxide, hydride, methyl, and methoxy terminated surfaces.](image)

**Figure 6.1** Functionalized SiNW arrays with corresponding linear scans of lithiation for native oxide, hydride, methyl and methoxy terminated surfaces. The onset potentials varied over a range of 400 mV with a scan rate of C (0.4166 mV/s).

Double differential charge versus potential plots for the ex situ functionalized SiNW array anodes are shown in Figure 6.2. The potential at which a drop in the double differential charge value is initiated during a shift resulting in a sign change, is considered to be the onset potential for lithiation. Native oxide shows the most anodic onset of the ex situ functionalized surfaces at 102 mV vs. Li/Li\(^+\). The native oxides also
show inhibited SEI layer formation, which is predominantly associated with chemical formation of lithium oxide near the anode surface, blocking the electrochemical electrolyte reduction reactions. Hydride termination is highly reactive with the dissociated electrolyte and forms an SEI layer. The hydride shows lithiation onset potential at \(-130\) mV vs. Li/Li\(^+\), nearly \(232\) mV more cathodic to native oxide, which may be due to mutual repelling forces between the positively charged hydride and lithium ions compared to the attractive forces between negatively charged oxide and positively charge lithium ions. Ex situ methyl (1:1 methyl: hydride coverage) functionalization inhibits the chemical reaction of the adjacent hydride group with the electrolyte due to steric effects, but may not completely eliminate the reaction. Ex situ methyl surface exhibits both electrical and chemical passivation, resulting in the most cathodic onset potential for lithiation at \(-320\) mV (vs. Li/Li\(^+\)), blocking lithium ion transport across the anode-SEI interface. Methoxy functionalization with 33\% surface coverage shifts the lithiation onset potential 92 mV cathodically relative to native oxide. It appears both 33\% methoxy (rest is oxide) and 1:1 methyl: hydride show more cathodic lithiation potentials relative to corresponding native oxide and hydride precursor anodes, implicating the methyl terminal group has a slightly repelling effect upon the lithium ions approaching the surface. This shows not only that the lithiation is a function of silicon surface chemistry, but also, more electronegative functional groups on the surface favors more lithiation of silicon. Although fluorine is the most electronegative functional group, silicon fluorides are highly unstable and also highly reactive with the electrolyte. Moreover inorganic fluorides may attack lithiated silicon alloy resulting in more capacity fade. Clearly, native oxide provides the most lithiation-favorable interface, but the SEI quality is relatively
weaker than the hydride. In this context, the native oxide terminated surfaces may be further functionalized via in situ electrolyte additive functionalizations in order to reinforce the SEI in addition to the interface.

![Double differential charge versus potential plots for ex situ functionalized native oxide, hydride, methyl and methoxy functionalized SiNW arrays. Plots were obtained by differentiating cyclic voltammograms shown in Figure 6.1.](image)

Figure 6.2 Double differential charge versus potential plots for ex situ functionalized native oxide, hydride, methyl and methoxy functionalized SiNW arrays. Plots were obtained by differentiating cyclic voltammograms shown in Figure 6.1.

6.3.2 Lithiation versus In situ Functionalization

Silicon lithiation is further investigated with in situ cross-linking siloxane or polymeric electrolyte additives to reinforce the SEI with native oxide termination. Trimethoxymethyl silane (M silane), triethoxyfluorosilane (F silane), vinylene carbonate (VC) and trifluoromethyl maleic anhydride (TFMMA) additives are used in this study. The cyclic voltammograms obtained with each of the in situ additives are shown in Figure 6.3 obtained at a scan rate of 0.04133 mV/s (C/10).
Figure 6.3 Linear scans showing SiNW lithiation with 5% triethoxyfluorosilane (F silane), 5% trimethoxymethyl silane (Methyl silane), 5% trifluoromethyl maleic anhydride (TFMMA) and 5% vinylene carbonate (VC) in situ functionalizations.

From Figure 6.3, M silane and F silane show chemical self-assembly, while VC and TFMMA show electrochemical deposition of a synthetic SEI, both resulting in reduced current density due to electrode passivation. The electrochemical nature of SEI formation in case of VC and TFMMA is characterized by the sharp cathodic peaks at higher potentials (1.2-1.5 V vs. Li/Li⁺). In contrast with M silane constituting a passive methyl group, F silane shows great reduction current throughout the window suggesting excellent cross-linking via reactive fluorine group; however, from Figure 6.3, both F silane and TFMMA show cathodic lithiation onset potentials outside the conventional cycling window of 1.5 to 0.01 V vs. Li/Li⁺, mainly due to excess presence of electrically insulative organofluorine based SEI layers. M silane shows the most anodic lithiation potential at ~0.1 V (vs. Li/Li⁺), while VC shows slightly more cathodic onset potential relative to M silane, at 50 mV (vs. Li/Li⁺). The M silane-SEI comprises chemical (self-
assembling silanes) and electrochemical (carbonate reduction) reaction products whereas VC SEI predominantly shows electrochemical reduction of the additive. In the previous chapter, in situ M silane functionalization is demonstrated to reinforce the silicon-SEI chemically and mechanically with silane cross-linking and Si-O-Si network in the SEI. Partial native oxide surface would enhance the M silane effect due to absence of insulative organofluorine compounds formed with the hydride surface and prompt instantaneous assembly of siloxane molecules over the native oxide interface. Ex situ native oxide, ex situ native oxide with in situ VC or M silane functionalized silicon-SEI are further investigated on SiNWs with direct electrical contact with Ni current collector via NiSi formation (NiSiNWs) to reinforce the electrical parameters of the interface.

6.3.3 NiSiNW Array Anodes

Pure nickel and NiSiNWs anodes are investigated via cyclic voltammetry and ex situ SEM imaging. Figure 6.4 shows the cyclic voltammograms of pure nickel and NiSiNWs anodes within the potential window of 1.5 V – 5 mV (vs. Li/Li+) obtained at a scan rate of 0.0208 mV/s (C/20). Pure nickel anodes show reduction peaks at ~0.55 V and ~0.2 V vs. Li/Li+ and a gradual increase in reduction current density below 0.2 V vs. Li/Li+. The peak at ~0.55 V may correspond to lithium ion adsorption on the nickel anode surface from the electrolyte, whereas the reduction current density at <0.2 V vs. Li/Li+ may be associated with lithium plating from counter electrode. NiSiNWs show greater hysteresis relative to pure nickel anodes mainly due to the excess current density with silicon-SEI formation. NiSiNW anodes also show a reduction peak stretching from ~0.55-0.2 V vs. Li/Li+, which may be ascribed to gradual lithium insertion into silicon forming saturated Li$_{22}$Si$_5$ alloy phase. The increase in current density at <0.2 V vs. Li/Li+
may be associated with underlying exposed nickel surface. Although discharge is not observed with any of the anodes due to very low quantities of nanowires relative to exposed nickel surface area resulting in negative reverse current densities; however, better discharge behavior may be expected with further cycling due to SEI passivation.

Figure 6.4 Charging behavior of pure Ni, bare, in situ VC functionalized, and in situ M silane functionalized NiSiNWs obtained at a scan rate equivalent to C/20 charging rate.

Ex situ SEM images are obtained for pure nickel and NiSiNWs to compare the SEI layer and NiSiNW morphology during cycling at scan rate of 0.0208 mV/s (C/20) after washing in pure DMC. Figure 6.5 shows the corresponding SEM images of charged nickel anodes (Figure 6.5 A), NiSiNW anodes before charging (Figure 6.5 B), after charging (Figure 6.5 C) and after discharging (Figure 6.5 D). Figures 6.5 A and 6.5 C show charged nickel and NiSiNW anodes containing pools of lithium on the surface. It appears that the lithium pools on NiSiNW anodes gradually get inserted into SiNWs.
expanding the nanowires as shown in the highlighted region in Figure 6.5 C. Figure 6.5 D shows the morphology of discharged NiSiNWs with amorphization of nanowires.

Figure 6.5 Scanning electron micrograph (SEM) images for A. charged pure nickel anodes, B. NiSiNW anodes before charging, C. charged NiSiNW anodes and D. discharged NiSiNW anodes.

The cycling characteristics of ex situ native oxide, in situ VC functionalized and in situ M silane functionalized NiSiNWs are compared via cyclic voltammetry plots obtained at a scan rate of C (0.41 mV/s) within the potential window of 1.5 V to 5 mV (vs. Li/Li$^+$) for multiple cycles.
6.3.4 Functionalized Silicon-SEI Interfaces – Cyclic Voltammetry

Silicon-SEI interfaces present the crucial barrier to lithium transport and by controlling the interface, anode lithiation may be improved. In this study, silicon-SEI interfaces of bare (ex situ native oxide terminated) NiSiNWs and in situ M silane functionalized NiSiNWs may be investigated via cyclic voltammetry at a fast scan rate of 0.4133 mV/s (~C). Figure 6.6 shows the cyclic voltammetry plots of ex situ native oxide terminated NiSiNWs over the later 25 cycles over the range of 1.5 V to 5 mV (vs. Li/Li⁺), as the first 5 cycles may be allowed for SEI formation. As expected, the voltammograms show gradual improvement in discharge capacities of the anode from 1 to 30 cycles. The gradual increase in discharge current density is mainly due to the SEI formation on the anode dominating the relatively low discharge current density during the initial cycles.

Figure 6.6 Cyclic voltammetry plots for bare NiSiNWs (native oxide terminated) within the potential window of 1.5 V to 5 mV vs. Li/Li⁺. Cycles 5, 10, 20 & 30 are shown, obtained at a scan rate of 0.4166 mV/s equivalent to C.
From Figure 6.6, lithiation and delithiation onset potentials are observed at ~0.4 V and 0.9 V vs. Li/Li$^+$ respectively during the cycles 5-30. The lithiation peak appears to shift anodically relative to SiNW arrays as the NiSiNWs have a low impedance, metallic nickel current collector instead of semi-conductive bulk silicon substrate in SiNW arrays with relatively higher impedance. Figure 6.7 shows the cyclic voltammetry of in situ 5% trimethoxymethyl silane functionalized NiSiNWs for 37 cycles obtained at a charging rate of 0.4133 mV/s (~C). The first five cycles may be allowed for SEI formation and the cycling behavior is shown from 6$^{th}$ to 37$^{th}$ cycles. The cycles from 6 to 37 show multiple reduction onsets at 0.9, 0.35 and 0.15 V (vs. Li/Li$^+$) corresponding to varying LiSi alloy phases of silicon lithiation.

Figure 6.7 Cyclic voltammetry plots for methyl silane (5% trimethoxymethyl silane) electrolyte additive functionalization within the potential window of 1.5 V to 5 mV vs. Li/Li$^+$. A. Cycles 1, 2 & 5. B. Cycles 6, 16, 25 & 37. Scan rate is 0.4166 mV/s equivalent to charging rate C.
The in situ silane functionalization also shows considerable silicon discharge current densities with anodic peaks at 0.35, 0.5, 0.95 V and ~1.5 V vs. Li/Li⁺; however, faster scan rate did not allow entire delithiation. The incomplete delithiation may be beneficial as the silane functionalized NiSiNWs show excellent capacity retention for at least 32 cycles (from cycles 6 – 37). In situ M silane functionalized NiSiNWs are encapsulated in a silicon-rich SEI layer with favorable chemical and mechanical properties as reported in the previous chapter. The direct electrical contact with underlying nickel current collector helped offer excellent electrical properties to the silicon-SEI rendering a near-perfect interface for silicon anode cycling. The interfaces of VC and F silane are also analyzed using cyclic voltammetry but both mimic the bare NiSiNW arrays and do not show any silicon discharge peaks. It appears in situ VC functionalization could not modify the NiSiNW-SEI considerably, due to the effect of conductive nickel current collector. F silane mimicked the cycling behavior of VC-functionalized and bare (ex situ native oxide terminated) NiSiNWs with steadily improving discharge behavior with a single significant discharge peak at ~0.9 V vs. Li/Li⁺ and does not show any silicon discharge peaks as displayed by in situ M silane. This result illustrates the Si-O-Si network in case of M silane provides the mechanical properties of the SEI whereas the methyl termination reinforces underlying silicon surface protection. In case of F silane, although Si-O-Si network improves the mechanical properties, extensive cross-linking due to fluorine group result in electrically insulative but a chemically reactive SEI layer blocking the lithium ion transport at the interface.
6.3.5 Functionalized Silicon-SEI Interfaces - Ex situ FTIR Spectroscopy

Ex situ FTIR spectroscopy is used to analyze synthetic SEI layer chemistry via in situ electrolyte additives. Figure 6.8 shows FTIR spectra for bare and M silane functionalized NiSiNWs.

Figure 6.8 Ex situ FTIR spectra for bare and in situ M silane functionalized NiSiNW anodes cycled for 32 and 37 charge/discharge cycles at a scan rate of 0.4133 mV/s (C).

Bare NiSiNWs show a large peak at 1092.4 cm\(^{-1}\) corresponding to lithium carbonate in the SEI. The same is confirmed by an asymmetric CO\(_2\) bending peak at 738.2 cm\(^{-1}\). Trace formation of lithium oxide is noticed at 785.3 cm\(^{-1}\), which may be due
to lithium ions reacting with bare, native oxide terminated NiSiNW surfaces. Lithium alkyl ether is another significant SEI product on bare NiSiNWs visible via peaks at 1161.4 and 1369.9 cm\(^{-1}\). The peaks observed at 1608.4 and 1633.9 cm\(^{-1}\) may correspond to lithium carboxylates (ROCO\(_2\)M\(^{n+}\)). Note the bare NiSiNWs in this study are native oxide terminated and electrically contacted on conductive nickel surfaces resulting in major peaks of lithium carbonate and lithium alkyl ether.

Ex situ FTIR with in situ trimethoxymethyl silane functionalization typically shows major peaks at 735.6 cm\(^{-1}\) corresponding to lithium carbonate, 1045.3 cm\(^{-1}\) due to Si-O group of Si-O-C silane molecule, 1164.3 cm\(^{-1}\) pointing to lithium alkyl ether and 1303 cm\(^{-1}\) related to Si-C formation. Peaks are also observed at 1460 cm\(^{-1}\) and 1664 cm\(^{-1}\) corresponding to lithium carbonate and C-F formation. A peak at 2974.3 cm\(^{-1}\) corresponds to a strong alkyl C-H bond related to presence of alkyl groups in silane and organic solvents. The ex situ FTIR results clearly show that the M silane provides the Si-O-Si network in SEI improving its chemical and mechanical aspects.

6.3.6 Functionalized Silicon-SEI Interfaces – Impedance Analysis

Impedance analysis may provide further insights into lithium diffusion through the functionalized SEI layers and silicon-SEI interfaces. A model electric circuit to a typical metallic anode consists of a solution resistance in series with an impedance element due to double layer capacitance and charge transfer resistance and impedance due to lithium diffusion through the anode. The impedance response in theory would comprise a perfect semicircle followed by a linear region corresponding to lithium diffusion. Balbuena et al. (Balbuena and Wang 2004), suggests SEI in lithium battery anodes usually consists of compact layers of molecules immediate to the surface of the
anode and porous, floppy layers of molecules toward the SEI-electrolyte interface. This would include additional semicircles to the typical anode response prior to the linear region. Huggins et al. (Huggins 2009) suggested the semicircles at lower frequencies specifically correspond to electronic impedance where as the ones at higher frequencies correspond to ionic impedance.

Figure 6.9 shows electrochemical impedance spectra taken for functionalized NiSiNW anodes after at least 20 charge/discharge cycles at a charging rate C. Nyquist spectra of bare and in situ functionalized NiSiNWs are used to analyze SEI electrical parameters suitable for capacity retention. The bare NiSiNW anodes in Figure 6.9 show a combination of an almost linear region at initial DC frequencies followed by a suppressed semicircle in the intermediate range and combination of two or more semicircles at high frequencies. At low frequencies, the electronic transport occurs through resistive pathways due to very high capacitive impedance. At high frequencies, a semicircle is typically observed for anodes corresponding to an active grain boundary with a double layer capacitance and offering charge transfer resistance.

M silane impedance spectra show an incomplete semicircle at around $Z' = 3000 \, \Omega$ followed by an almost linear region; however, the linear region is actually a combination of linear region and semicircle followed by another suppressed semi-circle similar to bare NiSiNWs. This indicates the silane shows saturated lithiation at low frequencies with a reduced double layer capacitance compared to that of bare NiSiNWs. The additional semicircle may be due to formation of a conductive SEI layer showing its own grain boundary layer with silicon nanowires. Also, Figure 6.9B shows at high frequencies, silane shows the least impedance corresponding to better ionic conductivity
relative to other functionalized and bare NiSiNW anodes. Although at low frequencies, vinylene carbonate and F silane show great electronic impedance relative to silane and bare NiSiNW anodes, it appears lithium conductivity mainly controls the cycling characteristics of the SEI.

Figure 6.9 Impedance analysis of bare and in situ silane functionalized NiSiNW anodes, A. Full frequency range from 1 mHz to 1 MHz; B. High frequency range from 1 MHz to ~10 Hz.
6.4 Conclusions

Silicon lithiation is demonstrated to be a function of both surface and SEI chemistries. SiNW array anodes are used to demonstrate different onset potentials for lithium adsorption with different surface terminal groups and in situ electrolyte additives. Native oxide termination shows better lithiation onset potential relative to hydride, methoxy and methyl groups. M silane shows more anodic onset than the in situ functionalization additives of VC, and F silane. SiNWs are further electrically contacted with underlying nickel metal current collector for better electrical interface. The NiSiNWs are allowed to form native oxide on the surface before in situ functionalized with VC, M silane and F silane electrolyte additives. Bare and in situ functionalized anodes are cycled for atleast 20 cycles each at a fast scan rate of C and as expected, M silane additive shows a significant reversible silicon discharge for atleast 32 cycles (From 6th to 37th cycles). Ex situ FTIR spectroscopy analysis reinforced the silane-rich SEI formation with M silane. As the initial polarity of Si-O-C result in silane self-assembling on silicon surface, the surface develops a new Si-Si-O-C termination emulating similar bond polarity between Si-O group. The bond polarity results in a continuous cross-linking of in situ silane molecules while anchored to the silicon anode substrate resulting in a compact SEI layer. Impedance analysis demonstrates M silane monolayers offer a compact Si-O-Si matrix with lower ionic impedance at high frequencies and higher electronic impedance at lower frequencies relative to other in situ additive functionalizations. The in situ methyl functionalization offer relatively better chemical, electrical and mechanical properties of the silicon-SEI interface resulting in better cycling characteristics of silicon anodes.
7. SUMMARY

Silicon surfaces were functionalized with unsaturated, reactive or self-assembling organic molecules to create passivating or reactive monolayers for specific applications. Electrochemical grafting technique was demonstrated to offer superior chemical and electrical quality monolayers. Thermal grafting techniques appear to apply excess energy to silicon surfaces resulting in random adsorbates and high surface roughness relative to electrografted monolayers. Alkyl monolayers functionalized via electrografting of Grignards offer better surface topography and passivation ability relative to those obtained via thermal two-step method. The anodically grafted alkyl monolayers were demonstrated to passivate the (100) surfaces against native oxide formation for ~55 days in ambient air. An anodic grafting mechanism is proposed to follow Grignard oxidation route via a two-electron process resulting in a 1:1 alkyl/hydride termination per each (100) silicon surface atom. The results provide an alternative to thermal oxidation of silicon and repeated toxic HF etch routes for gate dielectrics applications.

Electrochemistry for reducing unsaturated precursors such as phenylacetylene and 5-hexynoic acid were established via cyclic voltammetry. Cathodic grafting mechanism was explained in detail, where unsaturated precursor molecule loses an acidic proton to become reactive and attack the silicon hydride surfaces resulting in silyl radical formation. Another reactive unsaturated radical may attach to the silicon surface confirming a direct Si-C anchoring. The surface charge uptake calculations from cyclic voltammetry suggest the cathodic surfaces also show a 1:1 alkyne/hydride termination per each (100) silicon surface atom due to steric effects. In situ patterned electrografting via self-assembled polystyrene (PS) microspheres or 1:1 inverse or negative polydimethyl
siloxane (PDMS) stamps was demonstrated. The templates were observed to channel the electric field through the void spaces with electrolyte conductivity as one of the key resolution-limiting factors. The results suggest possible pathways to obtain molecular level feature sizes by controlling the template void space dimensions and electrolyte conductivity. Patterned 5-hexynoic acid surfaces were demonstrated to selectively immobilize biotin molecules via EDC chemistry. The result is interesting for antibody/antigen sensing applications providing an alternative to Enzyme-linked immunosorbent assay (ELISA) technique. Cathodic phenylacetylene and anodic methyl monolayers patterned via 1:1 inverse/negative PDMS stamps were demonstrated to channel copper electrodeposition specific to non-functionalized areas. Copper deposition was inhibited at nucleation step itself reinforcing the defect-free nature of the monolayers. The functionalization and nanoscale patterning techniques together could further provide novel inorganic-organic and inorganic-biological hybrid devices such as functionalized silicon anodes for lithium batteries, biosensors etc.

Direct or indirect functionalization techniques were used to investigate and identify the factors contributing to the capacity fade during cycling with silicon anodes in lithium batteries. The established anodic and cathodic grafting mechanisms were used to functionalize silicon nanowire based anodes for lithium batteries. Secondary lithium batteries operate at more cathodic potentials relative to unsaturated precursor reduction potentials. This provides a unique opportunity to apply in situ electrografted electrolyte additives on silicon anode surfaces for passivation against SEI species causing the fade. Further, silicon lithiation was observed to be a function of silicon anode surface chemistry. The result was used to demonstrate a silicon-rich SEI layer using in situ
alkoxy silane electrolyte additives, which inhibits the capacity fade in silicon nanowire based composite anodes. It appears that the alkoxy silane improves the chemistry and mechanical aspects of the silicon SEI due to the presence of silane cross-linking. Silicon lithiation was observed to be a function of in situ and ex situ surface functionalization. The result unlocks a wide range of organic functional groups to be investigated for better lithiation of anodes. The chemistry and electrical aspects of silicon nanowires-SEI was further analyzed with reinforced electrical contact to underlying nickel current collector. In situ alkoxy silane functionalization in combination with ex situ native oxide termination offered a significantly improved silicon-SEI interface with better chemical, mechanical and electrical aspects of the SEI. In future, the nickel-contacted nanowires may be used as anodes at higher scan rates. The results yielded better capacity retention along with a technique that can be implemented to any silicon based anodes in evolving lithium battery technologies such as lithium-polymer batteries or lithium-air batteries.
REFERENCES


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